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ANAEROBIC DIGESTION OF LIME SLUDGE.(U)  
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TECHNICAL REPORT 8205

ANAEROBIC DIGESTION OF LIME SLUDGE

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JULY 1982

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The purpose of this project was to determine the feasibility of using anaerobic digestion to treat sludges from the low-level lime addition process for phosphorus removal. Because digester supernatant is normally recycled to the influent of the sewage treatment plant, the re-release of any phosphorus is important. The operating characteristics of the digester using the lime sludge for fuel must be determined for process control and design.		

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20. Abstract (continued)

No significant amount of phosphorus was released into the digester supernatant; thus the phosphorus would be removed with the digester sludge for disposal.

The digesters were stably operated at a 27.5 day retention time but at a volatile solids destruction rate of 30 percent rather than the normal rate of 50 percent. Increasing levels of calcium were shown to cause progressive inhibition of the volatile solids destruction step in anaerobic digestion. Some synergistic effect was demonstrated with the calcium/magnesium pair. Sodium levels  $>1,000$  mg/L as Na resulted in a synergistic effect of the calcium/sodium ion pair. The methane formers appeared to be inhibited only by levels of sodium above 1,000 mg/L.

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## TABLE OF CONTENTS

ACKNOWLEDGMENT.....	1
INTRODUCTION.....	9
LITERATURE REVIEW.....	9
General Conditions.....	9
Organic Loading.....	10
Ammonia.....	10
Phosphorus.....	10
Heavy Metals.....	11
Light Metal Cations.....	11
MATERIALS AND METHODS.....	13
Sewage Source.....	13
Sludge Production.....	13
Digesters.....	15
Experimental.....	15
Analytical Methods.....	17
Gas Collection and Measurement.....	19
Feeding and Sampling Procedures.....	19
RESULTS.....	22
pH.....	22
Phosphorus.....	22
Ammonia.....	22
Volatile Acids.....	22
Gas Production.....	33
Heavy Metals.....	33
Alkalinity.....	33
Light Metal Cations.....	48
Volatile Solids Destruction.....	48
COD.....	48
DISCUSSION.....	68
pH.....	70
Phosphorus.....	70
Ammonia.....	71
Volatile Acids.....	71
Gas Productions.....	71
Loading.....	71
Heavy Metals.....	72
Volatile Solids Destruction.....	72
COD.....	81
CONCLUSIONS.....	82
REFERENCES.....	83
DISTRIBUTION LIST.....	86

## LIST OF FIGURES

1. Chemical Addition System.....	14
2. New Brunswick Model 19 Fermentors.....	16
3. Gas Collection System Used During Run 4.....	20
4. pH Profile for Run 1.....	24
5. pH Profile for Run 2.....	25
6. pH Profile for Run 3.....	26
7. pH Profile for Run 4.....	27
8. Volatile Acids Profile for Run 1.....	29
9. Volatile Acids Profile for Run 2.....	30
10. Volatile Acids Profile for Run 3.....	31
11. Volatile Acids Profile for Run 4.....	32
12. Daily Gas Production for Digester 1, Run 1.....	34
13. Daily Gas Production for Digester 2, Run 1.....	35
14. Daily Gas Production for Digester 3, Run 1.....	36
15. Daily Gas Production for Digester 1, Run 2.....	37
16. Daily Gas Production for Digester 3, Run 2.....	38
17. Daily Gas Production for Digester 1, Run 3.....	39
18. Daily Gas Production for Digester 2, Run 3.....	40
19. Daily Gas Production for Digester 3, Run 3.....	41
20. Daily Gas Production for Digester 1, Run 4.....	42
21. Daily Gas Production for Digester 2, Run 4.....	43
22. Daily Gas Production for Digester 3, Run 4.....	44
23. Average Total Alkalinity for Each Digester.....	46
24. Calcium Concentration vs. Alkalinity for Run 4.....	47
25. Potassium Profiles During Run 4.....	49
26. Sodium Profiles During Run 4.....	50



27. Magnesium Profiles During Run 4.....	51
28. Calcium Profiles During Run 4.....	52
29. Average Calcium Concentrations for Each Digester.....	53
30. Volatile Solids Destroyed vs. Volatile Solids Applied for Digester 2, Runs 1 and 3.....	54
31. Volatile Solids Destroyed vs. Volatile Solids Applied for Digesters 1 and 3, Run 1 9262-9313.....	55
32. Volatile Solids Destroyed vs. Volatile Solids Applied for Digesters 1 and 3, Runs 1 Through 3.....	56
33. Volatile Solids Destroyed vs. Volatile Solids Applied for Digesters 1 and 2, Run 4.....	57
34. Volatile Solids Destroyed vs. Volatile Solids Applied for Digesters 2 and 3, Run 4.....	58
35. COD Destroyed vs. COD Applied for Digesters 2 and 3, Run 4.....	59
36. Methane Produced vs. COD Applied for Digesters 1 Through 3, Run 4.....	60
37. Methane Produced per COD Applied vs. Alkalinity for Run 4.....	61
38. Percent Volatile Solids Reduction vs. Time from Start of the Run for Runs 1 through 3.....	69
39. Summary of Volatile Solids Destroyed vs. Volatile Solids Applied for Runs 1 through 3.....	75
40. Comparison of Volatile Solids Destroyed vs. Volatile Solids Applied for the Control Digesters.....	77
41. Comparison of Volatile Solids Destroyed vs. Volatile Solids Applied for Low Calcium Concentrations.....	78
42. Comparison of Volatile Solids Destruction vs. Volatile Solids Applied for High Calcium Concentrations.....	42
43. Percent Volatile Solids Destroyed vs. Total Alkalinity Based on an Average Loading of 5.24 Grams Volatile Solids per Day.....	80

## LIST OF TABLES

1. Effect of Ammonia Nitrogen on Anaerobic Digestion.....	11
2. Total Concentration of Individual Metals Required to Severely Inhibit Anaerobic Digestion.....	11
3. Stimulatory and Inhibitory Concentrations of Light Metal Cations.....	12
4. Synergistic and Antagonistic Cation Combinations.....	13
5. Lime Sources and Quality for Use in the Chemical Addition System.....	15
6. Sample Schedule for Runs 1 through 3.....	18
7. Sample Schedule for Run 4.....	18
8. Duration of Runs 1 through 4 and Cation Contents for Digesters 1 Through 3.....	23
9. Average Soluble Phosphorus Concentrations.....	28
10. Average Ammonia-Nitrogen Concentrations.....	28
11. Average CO <sub>2</sub> Gas Composition During Run 4.....	33
12. Heavy Metals in Digester Effluents at the End of Run 3.....	45
13. Average Heavy Metal Concentrations in Digester Effluents During Run 4.....	45
14. Summary of Least Squares Analysis of Volatile Solids Destroyed vs. Volatile Solids Applied During Runs 1 through 4.....	62
15. Statistical Comparison of Slopes and Intercepts Using the Analysis of Variance Technique for Volatile Solids Destruction During Runs 1 through 3.....	63
16. Statistical Comparison of Slopes and Intercepts Using the Analysis of Variance Technique for Volatile Solids Destruction During Run 4.....	64
17. Summary of Composite Lines from the Statistical Comparison of Slopes and Intercepts of Volatile Solids Destruction During Runs 1 through 3.....	65
18. Summary of Least Squares Analysis of COD Destroyed vs. COD Applied During Run 4.....	65
19. Statistical Comparison of Slopes and Intercepts Using the Analysis of Variance Technique for COD Destruction During Run 4.....	66
20. Summary of Least Squares Analysis of Methane Produced vs. COD Applied During Run 4.....	67

21. Summary of Least Squares Analysis of Methane Produced per COD Applied vs. Total Alkalinity During Run 4.....	67
22. Preliminary Cation Scan at the End of Run 3.....	73

## INTRODUCTION

Increasingly strict effluent phosphorus limitations have resulted in renewed research into phosphorus removal processes. One process being considered is low-level lime addition to primary clarifiers.<sup>1,2</sup> This method of phosphorus removal will result in large quantities of primary sludges containing high concentrations of lime and its reaction products.

Anaerobic digestion is one of the most cost effective methods of sludge stabilization, particularly with today's rising energy costs. The Army employs anaerobic digestion for sludge stabilization in many waste treatment plants. Any decrease in the rate of solids destruction in the anaerobic digestion process can result in significantly higher digester volume requirements. The characteristics of lime sludge degradation were researched to determine the feasibility of using this technique with existing equipment to handle the lime sludge resulting from phosphorus removal.

In order to determine the feasibility of using anaerobic digestion on lime sludges, the extent of biodegradation must be defined in view of the following considerations:

1. The stabilized sludge must be of acceptable quality for disposal for the anaerobic digestion process to be feasible.
2. Since supernatant return to the head of the plant is a standard procedure for digester operation, the re-release of phosphorus within the digester is of prime importance.
3. The lime coagulation process may concentrate metals or organic compounds within the digester that could inhibit the process or prove to be toxic.
4. Finally, the conditions for digestion of sludges resulting from the low-level lime addition process for phosphorus removal must be defined for process control.

## LITERATURE REVIEW

### GENERAL CONDITIONS

The process of anaerobic digestion may be considered to occur in three stages. The first stage is hydrolysis of solid organic matter by extracellular enzymes.<sup>3,4</sup> After the solid matter is broken down into relatively short chains (sugars, starches, fatty acids, and proteins), the acid formers then produce volatile organic acids, primarily acetic and propionic acids plus other small organic compounds, from the remains of the organic matter. The organisms that comprise the acid former population are many and varied. In essence the acid formers are a group of symbiotic organisms that eventually produce acetic and propionic acids as the predominant end products.<sup>5</sup> The third and final stage is methane formation. Methanogenic bacteria convert short-chain organics, primarily acetic acid, to methane ( $\text{CH}_4$ ) and carbon

dioxide ( $\text{CO}_2$ ).<sup>5</sup> However, other compounds, such as formic acid, propionic acid, butyric acid, ethanol, acetone, leucine, valine, and stearic acid, can be converted to  $\text{CH}_4$ .<sup>6-8</sup>

The acid formers and methane formers live in a delicate balance. In order for the process to be stable, the rate of acid production must be equal to or less than the rate of acid conversion to methane. If the acids begin to accumulate, the pH will drop and cause digester failure. Prior to 1960 volatile acid concentrations greater than 2,000 mg/L as acetic acid were considered to be toxic to anaerobic digesters; however, in the early 1960's McCarty and associates performed controlled studies on volatile acid additions and these results showed that acid concentrations of up to 6,000-8,000 mg/L as acetic acid could be maintained and not be toxic to the methane formers, provided the pH be maintained between 6.6 to 7.4.<sup>9</sup> Digester failure may also occur at high pH due to ammonia or perhaps unionized volatile acid toxicity.

Anaerobic digesters are normally operated in the mesophilic range of 90° to 110°F (32° to 43°C) but are extremely sensitive to temperature change.<sup>5</sup> Stable digester operation usually requires temperature changes not to exceed 1°F per day.

#### ORGANIC LOADING

If the organic loading were suddenly increased, excess substrate for the acid formers would be present. As the availability of food is increased, the rate of cell production and acid former population will increase. Since the rate of acid formation is dependent upon the microbial population, more acid will be produced and as more acid becomes available, the methane formers will reproduce more rapidly. This rapid growth leads to a serious problem. The average growth rate for the methane formers is considerably slower than the average growth rate for acid formers.<sup>10</sup> Because of the growth rate imbalance, the volatile acids will tend to accumulate in the system after an organic shock load, resulting in digester upset and failure.<sup>9,11-13</sup> Typical design volatile solids loadings for mesophilic, high rate anaerobic digesters are from 0.15 to 0.40 pounds of volatile solids per day per cubic foot of digester capacity (2,400 to 6,400 grams per cubic meter per day).

#### AMMONIA

Ammonia toxicity is a common cause of digester failure.<sup>9,14-16</sup> Ammonia in high concentrations or at high pH has been shown to be toxic or inhibitory to anaerobic digestion. The effect of ammonia on anaerobic digestion is shown in Table 1.

#### PHOSPHORUS

Lime addition is a proven method for phosphorus removal.<sup>1,2</sup> After lime addition, phosphorus is considered to be in the form of calcium hydroxyapatite ( $\text{Ca}_5-(\text{OH})(\text{PO}_4)_3$ ), which will not resolubilize under digester conditions.<sup>9,17</sup> Thus, it is expected that supernatant return from the digesters will not add a significant phosphorus load to the plant influent. In Newmart, Ontario, addition of lime to the primary clarifiers for phosphorus removal and subsequent digestion of the lime sludge resulted in a decrease of phosphorus in the digester supernatant from 150 mg/L  $\text{PO}_4\text{-P}$  when digesting raw primary sludge to 4 mg/L  $\text{PO}_4\text{-P}$  when digesting primary lime sludge.<sup>18</sup>

TABLE 1. EFFECT OF AMMONIA NITROGEN  
ON ANAEROBIC DIGESTION<sup>9</sup>

Concentration mg/L NH <sub>3</sub> -N	Effect
50-200	Beneficial
200-1,000	No adverse effects
1,500-3,000	Inhibitory at pH over 7.4-7.6
Above 3,000	Toxic

#### HEAVY METALS

A variety of heavy metals have been shown to be inhibitory or toxic to anaerobic digestion.<sup>9,19-23</sup> Concentrations of heavy metals inhibitory to anaerobic digestion are given in Table 2. It should be noted that in order to be toxic the heavy metals must be in soluble form.

TABLE 2. TOTAL CONCENTRATION OF INDIVIDUAL METALS  
REQUIRED TO SEVERELY INHIBIT  
ANAEROBIC DIGESTION<sup>9</sup>

Metal	Metal % of Dry Solids	mg/L at 4% Dry Solids	Soluble Metal mg/L
Copper	0.93	372	0.5
Cadmium	1.08	432	-
Zinc	0.97	388	1.0
Iron	9.56	3,824	-
Chromium <sup>6+</sup>	2.20	880	3.0
Nickel	-	-	2.0

#### LIGHT METAL CATIONS

Work done in the early 1960's has shown that the light metal cations (calcium, magnesium, potassium, and sodium) are capable of causing stimulatory, inhibitory or toxic effects in anaerobic digesters.<sup>14-16,19,20,24-26</sup>

These cations are of little concern in the digestion of sludges from municipal or domestic waste treatment; however, the addition of large amounts of calcium and magnesium to the sludges during lime treatment for phosphorus removal results in concern about the effects of these cations on digester performance.

In the studies carried out by Kugelman and McCarty,<sup>15,25,26</sup> it was found that calcium and magnesium were toxic to the methanogenic bacteria, causing 50 percent reductions in acetic acid utilization rate at slug doses of 0.11 M (4,400 mg/L Ca) and 0.08 M (1,900 mg/L Mg), respectively. It was also found that gradual accumulation of these cations caused inhibition at higher concentrations. Sodium and/or potassium were found to produce antagonism to calcium and magnesium inhibition at concentrations of 0.002 M (46 mg/L Na and 98 mg/L K). In addition, calcium and magnesium were found to be synergistic at magnesium concentrations as low as 0.002 M (48 mg/L Mg). These studies were carried out in carefully controlled substrates with enrichment cultures of methanogenic bacteria only. It is anticipated that in the extremely complex substrates (sludge), complex interactions between antagonistic and synergistic compounds will occur. Also, significant variations from these cation concentrations and the cation concentrations summarized in Table 3 may occur.

The US Environmental Protection Agency (USEPA) has summarized work done on cation toxicity.<sup>9</sup> Concentrations of cations found to be stimulatory and inhibitory are shown in Table 3.

TABLE 3. STIMULATORY AND INHIBITORY CONCENTRATIONS OF LIGHT METAL CATIONS<sup>9a</sup>

Cation	Concentration (mg/L)		
	Stimulatory	Moderately Inhibitory	Strongly Inhibitory
Calcium	100-200	2,500-4,500	8,000
Magnesium	75-150	1,000-1,500	3,000
Potassium	200-400	2,500-4,500	12,000
Sodium	100-200	3,500-5,500	8,000

a. For acetate-utilizing methanogenic bacteria.

It should be noted that the concentrations given in Table 3 are for single cation effects on acetate-utilizing methanogenic bacteria only. Large variations in effect at a given concentration may be expected in complex substrates. The synergistic and antagonistic cation combinations are summarized in Table 4. The information presented in Table 4 was derived from acetate-utilizing cultures of methanogenic bacteria and may be assumed to be applicable only to these organisms.

TABLE 4. SYNERGISTIC AND ANTAGONISTIC  
CATION COMBINATIONS<sup>9a</sup>

Toxic Cations	Synergistic Cations	Antagonistic Cations
Ammonium	Calcium, magnesium, potassium	Sodium
Calcium	Ammonium, magnesium	Potassium, sodium
Magnesium	Ammonium, calcium	Potassium, sodium
Potassium	--	Ammonium, calcium, magnesium, sodium
Sodium	Ammonium, calcium, magnesium	Potassium

a. For acetate-utilizing methanogenic bacteria.

#### MATERIALS AND METHODS

##### SEWAGE SOURCE

The raw sewage source for this project was from the collection system serving the housing areas at Fort Detrick, Frederick, Maryland. A Moyno Grinder Pump <sup>®</sup> was located in a manhole downstream from the Fort Detrick housing area and upstream from the various chemical and microbiological laboratories located at Fort Detrick. Therefore, the sewage was strictly of a domestic origin.

##### SLUDGE PRODUCTION

Domestic sewage was pumped at 7.5 gpm into a grit chamber (retention time 33 min) equipped with a grease trap. Following the grit chamber was a 375 gal circular clarifier with a surface overflow rate of 859 gpd/ft<sup>2</sup>, a weir overflow rate of 859 gpd/ft, and a retention time of 50 min. Sludge for the control digester was taken from the primary clarifier.

Effluent from the grit chamber was pumped at 1.5 L/min through a chemical addition system (Fig. 1) to produce the lime sludge. The chemical addition system consisted of a rapid mix unit having a 5 min retention time, a flocculation unit having a 50 min retention time, a clarifier having a weir overflow rate of 115 gpd/ft and surface overflow rate of 75 gpd/ft<sup>2</sup>, and a 30 gal continuously mixed lime holding tank. A Chemtrix Model 47 pH controller maintained the pH in the flocculator at 9.5 to simulate the low-level lime addition process for phosphorus removal. The lime sludge was removed daily. An identical sludge production system was used during run 4 to produce sludge from a reagent grade lime. Table 5 presents the characteristics of the two grades of lime used during the project.



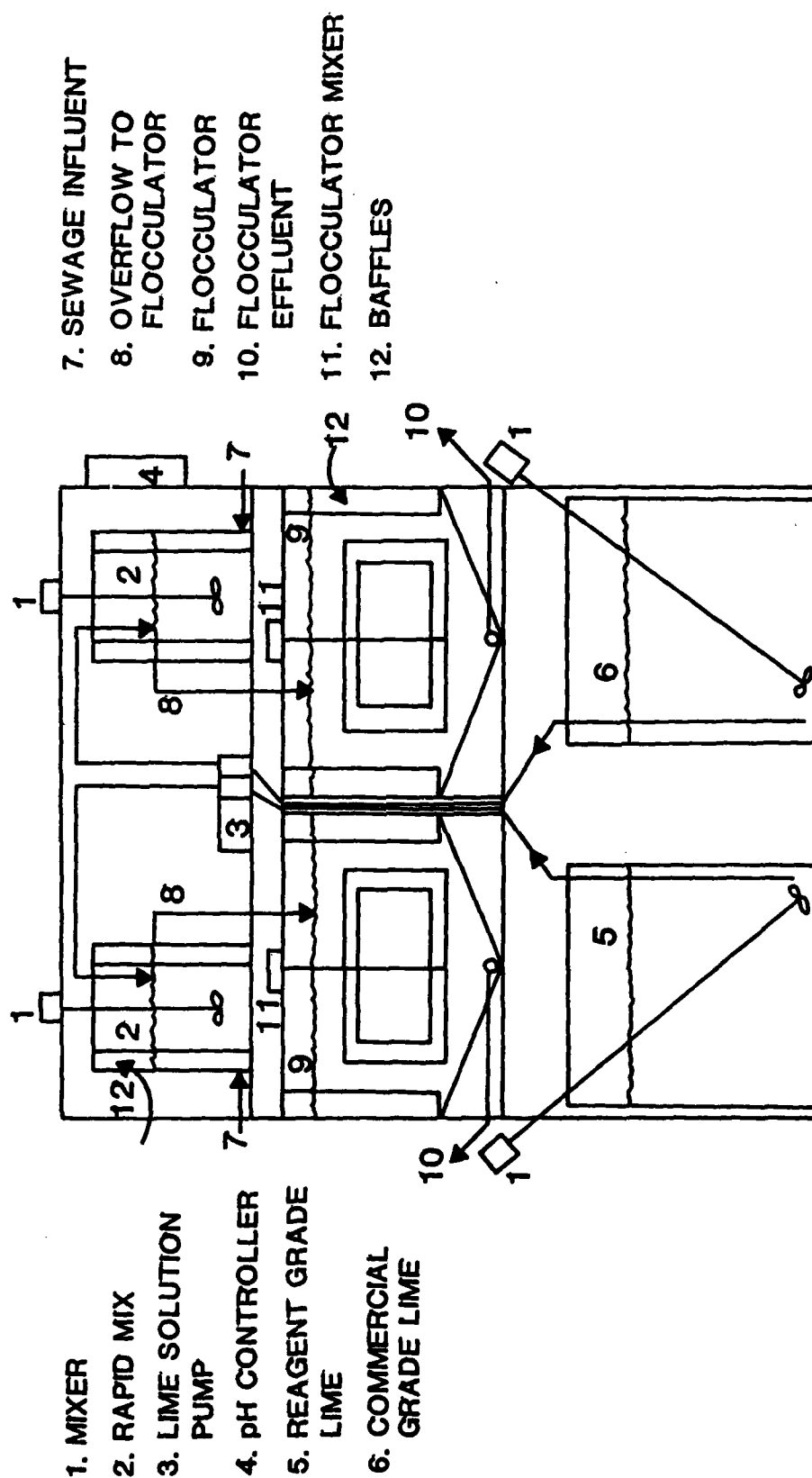


Figure 1. Chemical addition system.

TABLE 5. LIME SOURCES AND QUALITY FOR USE  
IN THE CHEMICAL ADDITION SYSTEM

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1. Calcium Hydroxide Powder (Reagent Grade)	
U.S.P. - F.C.C., Food Grade	
J.T. Baker Company	
2. Hydrated Lime (commercial grade) Guaranteed Quality	
Min. calcium oxides	71.00%
Min. magnesium oxides	1.00%
Min. total oxides	72.00%
Calcium hydroxide	93.00%
Max. oxides of calcium and magnesium present as carbonates	
As carbonates	1.00%
E.N.P.	1.29
CaO equivalent	71.00%

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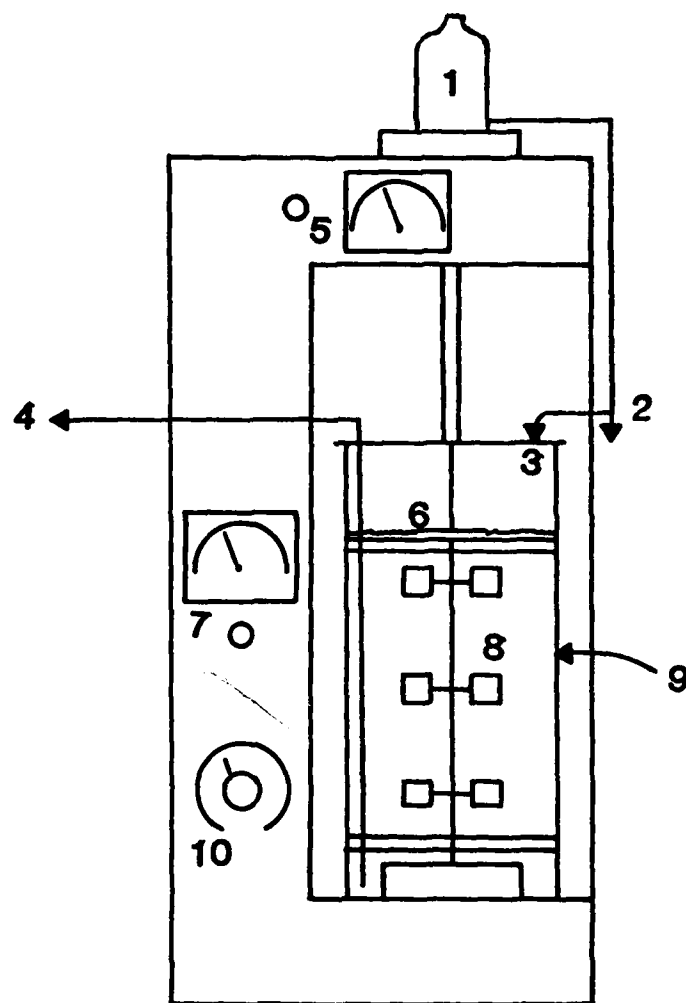
Sludges for the digesters were produced and collected daily during runs 1 through 3. Sludge production for run 4 was done in batches lasting approximately 20 days before the next batch was produced. These batches were stored in 20 L containers and refrigerated at 4°C. Each batch was adjusted by gravity thickening or water dilution as necessary to adjust the organic strength of the sludge. Variations in feed strength did occur during run 4; however, the large oscillations in feed sludge quality that were present in runs 1 through 3 were greatly reduced.

#### DIGESTERS

Three New Brunswick Scientific Company Model 19 Fermentors with foam breaker were used as anaerobic digesters (Fig. 2). Each digester was maintained at 35°C throughout the study. With a working volume of 11 L, a 27.5 day retention time was maintained. Continuous mixing was sustained through internal agitation, and a constant speed of 200 rpm was maintained for the turbine impellers. The foam breaker impeller speed was kept constant at 600 rpm.

#### EXPERIMENTAL

Three digesters were run in parallel for all four runs. The digesters were seeded with actively digesting anaerobic sludge from the wastewater treatment plant in Hagerstown, MD. Raw primary sludge was fed to all three digesters during start-up, until the volatile acid concentration became steady (200-800 mg/L as acetic acid). Gradually digesters 1 and 3 were fed increasing amounts of lime sludge mixed with the primary sludge, until only lime sludge was being introduced as the feed material. Digester 2 served as the control unit and was fed only primary sludge.



1. COMPLETELY MIXED FEED JUG
2. FEED SAMPLE PORT
3. FEED INLET PORT
4. EFFLUENT LINE
5. FOAM BREAKER SPEED CONTROL
6. FOAM BREAKER
7. TURBINE IMPELLER SPEED CONTROL
8. TURBINE IMPELLER
9. 11 LITER FERMENTOR VESSEL
10. TEMPERATURE CONTROL

Figure 2. New Brunswick Model 19 fermentors.

All reactor effluent not used for sample analysis was saved and kept active in sealed 5-gal carboys at room temperature. At the end of runs 1 and 2, the saved sludge was mixed with the contents of all three digesters. The digesters were then reloaded and start-up was initiated. The mixing of the sludges served to upset the digesters between runs 2 and 3 to see if the same volatile solids destruction would be achieved and to determine if any toxic substances might accumulate during the study. Run 1 was considerably longer than runs 2 and 3 in order to determine if any build-up of toxic substances occurred.

After run 3, an evaluation of the data showed that an inhibitory effect persisted throughout runs 1 through 3. Run 4 was designed to define the cause of the inhibition. All three digesters for run 4 were restarted with anaerobic sludge from the Hagerstown sewage treatment plant. Digester 2 remained the control. Since a synergistic effect between calcium and magnesium was suspected, digester 1 was fed a lime sludge with magnesium impurities in the lime (commercial grade lime), and digester 3 was fed a lime sludge made from reagent grade lime. If magnesium produces a synergistic effect with calcium, a lower volatile solids destruction rate would be expected. In an attempt to reverse the inhibition, sodium bicarbonate ( $\text{NaHCO}_3$ ) was added to digesters 1 and 3 near the end of run 4. Sodium when added to a calcium and/or magnesium solution has been shown to act as an antagonist in methanogenic cultures.<sup>9,15</sup>

#### ANALYTICAL METHODS

Samples were analyzed by USAMBRDL chemistry personnel. The sample schedule is presented in Table 6 for runs 1 through 3 and in Table 7 for run 4. The procedures for the tests are as follows:

Total Solids: Standard Methods<sup>27</sup> Part 208A

Total Volatile Solids: Standard Methods<sup>27</sup> Part 208E

Ammonia Nitrogen: Standard Methods<sup>27</sup> Part 418A for preliminary distillation and Part 413 J for electrode analysis

Soluble Phosphorus: Standard Methods Part 425A, preliminary filtration; Part 425C, Digestion; and Part 425D, Colorimetric Method

Total Alkalinity: Standard Methods Part 403 for runs 1 through 3; Arm and Hammer Method<sup>28</sup> for run 4

Volatile Acids: Gas Chromatography<sup>29</sup>, runs 1 through 3; Arm and Hammer Method<sup>28</sup>, run 4

Light Metal Cations: EPA<sup>30</sup> Atomic Absorption

Heavy Metals: EPA<sup>30</sup> Atomic Absorption

CO<sub>2</sub>: Orsat analysis for CO<sub>2</sub>

TABLE 6. SAMPLE SCHEDULE FOR RUNS 1 THROUGH 3

Test	Sun	Mon	Tue	Wed	Thu	Fri	Sat
Total solids	-	X <sup>a</sup>	X	X	X	X	-
Volatile solids	-	X	X	X	X	X	-
Ammonia	-	X	X	X	X	-	-
Soluble phosphorus	-	-	X	-	X	-	-
Total alkalinity	-	X	-	X	-	X	-
Volatile acids	-	X	-	X	-	X	-
pH	X	X	X	X	X	X	X

a. X = The day when the analysis was performed.

TABLE 7. SAMPLE SCHEDULE FOR RUN 4

Test	Sun	Mon	Tue	Wed	Thu	Fri	Sat
Total solids	-	X <sup>a</sup>	X	X	X	X	-
Volatile solids	-	X	X	X	X	X	-
Chemical oxygen demand	-	X	X	X	X	X	-
Soluble phosphorus	-	-	X	-	X	-	-
Ammonia	-	X	-	X	-	X	-
Total alkalinity	-	X	X	X	X	X	-
Volatile acids	-	X	X	X	X	X	-
Light metal cations	-	X	-	-	-	-	-
Orsat CO <sub>2</sub>	X	X	X	X	X	X	X
CH <sub>4</sub> gas chromatography	-	X	-	X	-	X	-
pH	X	X	X	X	X	X	X

a. X = The day when the analysis was performed.

The methane percentage was measured on a gas chromatograph using an FID detector and a Carbo Pack® C/O 0.3% CW 20 M/0.1% H<sub>3</sub>PO<sub>4</sub> column. A calibration curve was prepared each day from a pure methane standard. The chart response from each unknown sample was compared to that day's calibration curve, and the methane percentage was determined. The samples were collected by displacing a water/H<sub>2</sub>SO<sub>4</sub>/salt solution in a sample bottle. The injection sample was taken from the sample bottle without introducing any air into the system. The GC analysis of the gas percentages served as a control for the Orsat<sup>2</sup> analyzer. The GC analysis gave the percent methane. The CO<sub>2</sub> percentage was determined by difference. The differences in CO<sub>2</sub> percentages were always within 1 or 2 percentage points (well within experimental error).

#### GAS COLLECTION AND MEASUREMENT

During the first three runs, two Precision Scientific wet test meters were used to measure gas production for digesters 1 and 2. Gas from digester 3 was collected in a water displacement system. Before the commencement of run 4, a new water displacement gas collection system was built for each reactor (Fig. 3) to facilitate gas sampling.

The gas collection system shown in Figure 3 consisted of six inverted 1,000 mL graduated cylinders submerged in a plexiglass tank with interior dimensions of 39 15/16 in by 10 1/16 in by 14 in. The graduated cylinders were connected by a manifold. The manifold allowed the gas from all six cylinders to feed simultaneously into the gas sampling bottles. As the gas cylinders were filled, the water level in the tank would rise. The change in the water level in the tank was much less than the change in the water level in each column. When an observed volume of 4 L of gas was collected the tank water level would rise 0.66 in, while the water level in the graduated cylinders would drop 9.2 in. Using a pressure correction factor on the observed volume, the system was calibrated and a 3 percent error was observed.

#### FEEDING AND SAMPLING PROCEDURES

The daily feeding and sampling procedures were as follows for runs 1 through 3:

- (1) The lime sludge and primary sludge were collected and sampled.
- (2) The gas volume measurements were taken, and time was recorded.
- (3) The agitator speed was increased from 200 to 500 rpm for 5 min before sampling to ensure that complete mix conditions were achieved and to break up any deposits of solids on the bottom or walls of the reactors.
- (4) The ambient temperature was recorded to allow correction of the gas volumes to standard temperature and pressure (STP).
- (5) Between 400 and 500 mL of the contents of each digester was pumped into a separate beaker. As the digested sludge was being pumped into each beaker, the pH was measured.
- (6) Samples of the reactor effluent were then taken for analysis.

1. GAS INLET
2. GAS OUTLET
3. 1000 mL GRADUATED CYLINDERS
4. SULFURIC ACID / WATER SOLUTION
5. DRAIN
6. TANK LIQUID LEVEL
7. CYLINDER WATER LEVEL

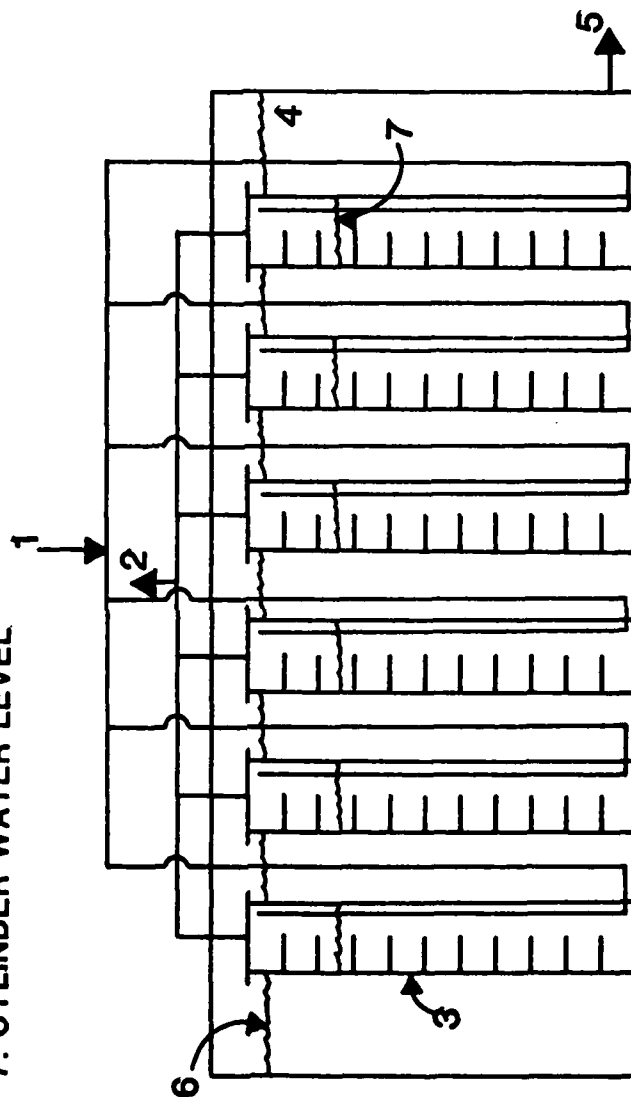


Figure 3. Gas collection system used during run 4.

(7) The feed pH was adjusted as necessary.

(8) The feed lines were charged with the feed sludge to minimize the amount of air introduced into the system. Four hundred milliliters of sludge were pumped into the reactor; any excess effluent that was withdrawn (more than 400 mL) was pumped back into the reactor to maintain digester volume.

(9) The portion of the effluent left from the original 400 mL, after taking samples, was stored in a 5-gal carboy at room temperature to be used as seed sludge for the next run.

(10) The wet test meters were read again to give an initial gas volume. The gas was vented out of the water displacement system.

(11) The feed and effluent lines to the digesters were cleaned each day.

The daily feeding and sampling procedures were slightly different for run 4.

(1) The gas volume measurements and ambient temperature readings were taken, and the time was recorded.

(2) The agitator speed was increased from 200 to 500 rpm for at least 5 min to ensure that complete mix conditions were achieved and to break up any solids deposits on the bottom or walls of the reactor.

(3) Four hundred milliliters of effluent were withdrawn. As the digested sludge was being pumped into a beaker, the pH was measured.

(4) Each beaker, containing 400 mL of sludge, was stirred vigorously, and while stirring a sample of the sludge was taken for analysis.

(5) The feed sludge pH was measured and adjusted with the appropriate lime as necessary.

(6) Approximately 1 L of feed sludge was transferred to a volume calibrated aspirator bottle on top of each digester (Fig. 2). A magnetic mixer was used to keep the feed completely mixed.

(7) The drain valve on the feed line to the digester was opened to allow the feed line to fill (displacing as much air as possible).

(8) A sample of each feed sludge was taken from the feed drain valve.

(9) The feed volume in the aspirator bottle was then lowered to the 400 mL mark. While stirring continued in the aspirator bottle, a pinch clamp on the line going into the reactor was opened, allowing 400 mL of feed to be introduced into the digester via gravity flow.

(10) The remainder of the feed sludge was returned to the 20 L container and again refrigerated.

(11) The feed system and effluent lines were cleaned with water.



(12) Gas collection bottles were filled with a salt-saturated 1 M  $\text{H}_2\text{SO}_4$ /water solution (the same solution was used in the gas collection system to prevent absorption of  $\text{CO}_2$  and  $\text{CH}_4$  into water). The connecting tubing lines were also filled with the salt/ $\text{H}_2\text{SO}_4$ /water solution.

(13) The pressure release valve was opened, and the gas displaced the water solution from the gas sampling bottles. The sample bottles were sealed.

(14) Onsite analysis for  $\text{CO}_2$  was performed using an Orsat analyzer. A second sample was analyzed on a gas chromatograph for  $\text{CH}_4$ .

(15) The remaining gas in the collection system was bled off, and the system was reset for the next day's gas collection.

### RESULTS

Three digesters were operated in parallel for each run. Four consecutive runs were made between August 1979 and May 1981. Table 8 presents the duration of each run and status of each reactor.

#### pH

The pH of each reactor was monitored daily. The pH profile of each reactor during runs 1 through 4 is presented in Figures 4 through 7. The pH in all cases remained in the 6.7 to 7.3 range. The pH in reactors 1 and 3 of run 4 increased gradually during the period Julian dates 1075 to 1110. Sodium addition began on Julian date 1075 and continued to the end of the study. (Note: For Julian dates the first digit denotes the year, and the last three digits denote the day of the year, e.g., 1075 is the 75th day of 1981.)

#### PHOSPHORUS

Soluble phosphorus was monitored in the digester feed and effluent in order to evaluate resolubilization of phosphorus during digestion. The average soluble phosphorus concentrations for the feed and effluent are presented in Table 9.

#### AMMONIA

Ammonia was monitored in both the reactor feed and the effluent. The average ammonia concentrations for the reactor feed and effluent are presented in Table 10.

#### VOLATILE ACIDS

The volatile acids within each reactor were monitored and used as an indicator of process stability. Profiles of the volatile acids for runs 1 through 4 as a function of time are presented in Figures 8 through 11, respectively. The volatile acids concentration generally remained below 500 mg/L as acetic acid. Required maintenance on the internal bearings of the fermentors resulted in process upset due to oxygen toxicity. A rise in volatile acid concentration was observed immediately after each required bearing maintenance.

TABLE 8. DURATION OF RUNS 1 THROUGH 4 AND CATION CONTENTS  
FOR DIGESTERS 1 THROUGH 3

Run	Digester 1		Digester 2		Digester 3	
	Julian Date	Cation Content	Julian Date	Cation Content	Julian Date	Cation Content
1	9261-9313	Low Ca <sup>a</sup>	9261-0008	Control	9261-9313	Low Ca
1	9314-0008	High Ca <sup>b</sup>			9314-0008	High Ca
2	0050-0099	High Ca	0050-0099	Control	0050-0099	High Ca
3	0125-0192	High Ca	0125-0191	Control	0125-0190	High Ca
4	0291-0338	Low Ca	0294-1126	Control	0312-1023	Low Ca
4	0343-1073	High Ca			026-1072	High Ca
4	1075-1104	High Ca <1,000 mg/L Na			1075-1104	High Ca <1,000 mg/L Na
4	1105-1126	High Ca >1,000 mg/L Na			1105-1126	High Ca >1,000 mg/L Na

a. Low Ca = less than 8,000 mg/L Ca.

b. High Ca = greater than 8,000 mg/L Ca.

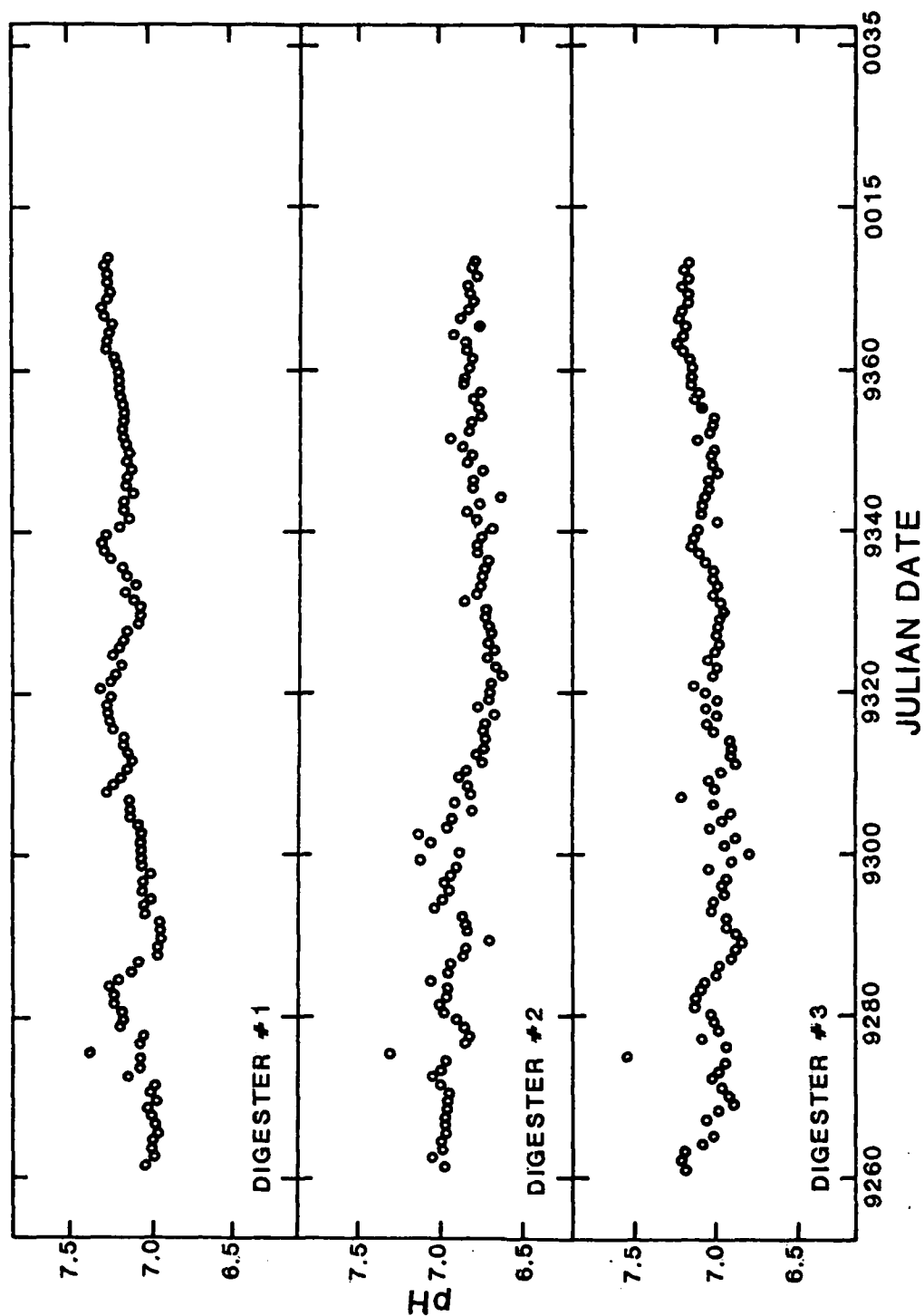


Figure 4. pH Profile for run 1. Commercial grade lime was used to make sludge for digesters 1 and 3. Digester 2 was the control unit.

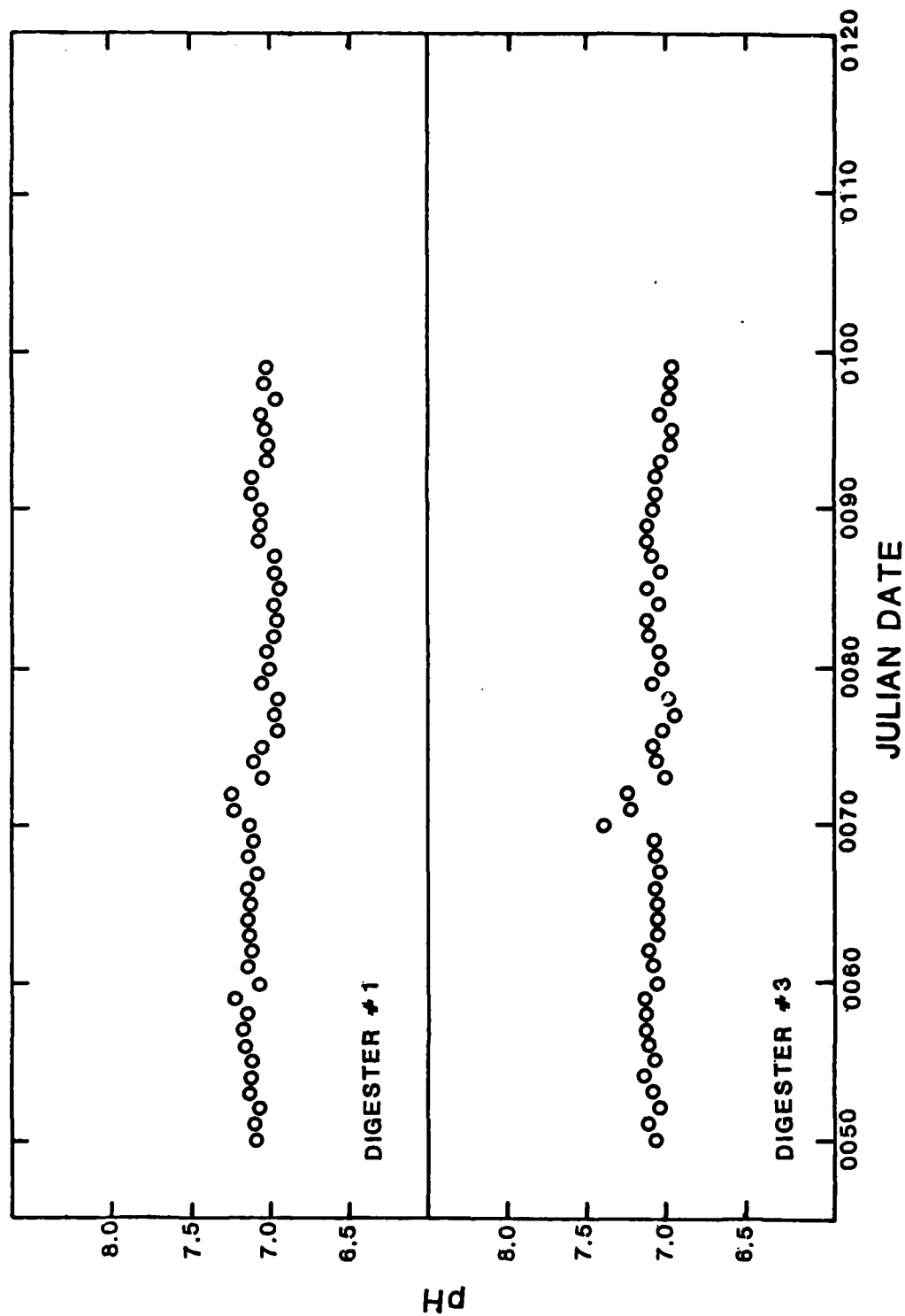


Figure 5. pH Profile for run 2. Commercial grade lime was used to make sludge for digesters 1 and 3.

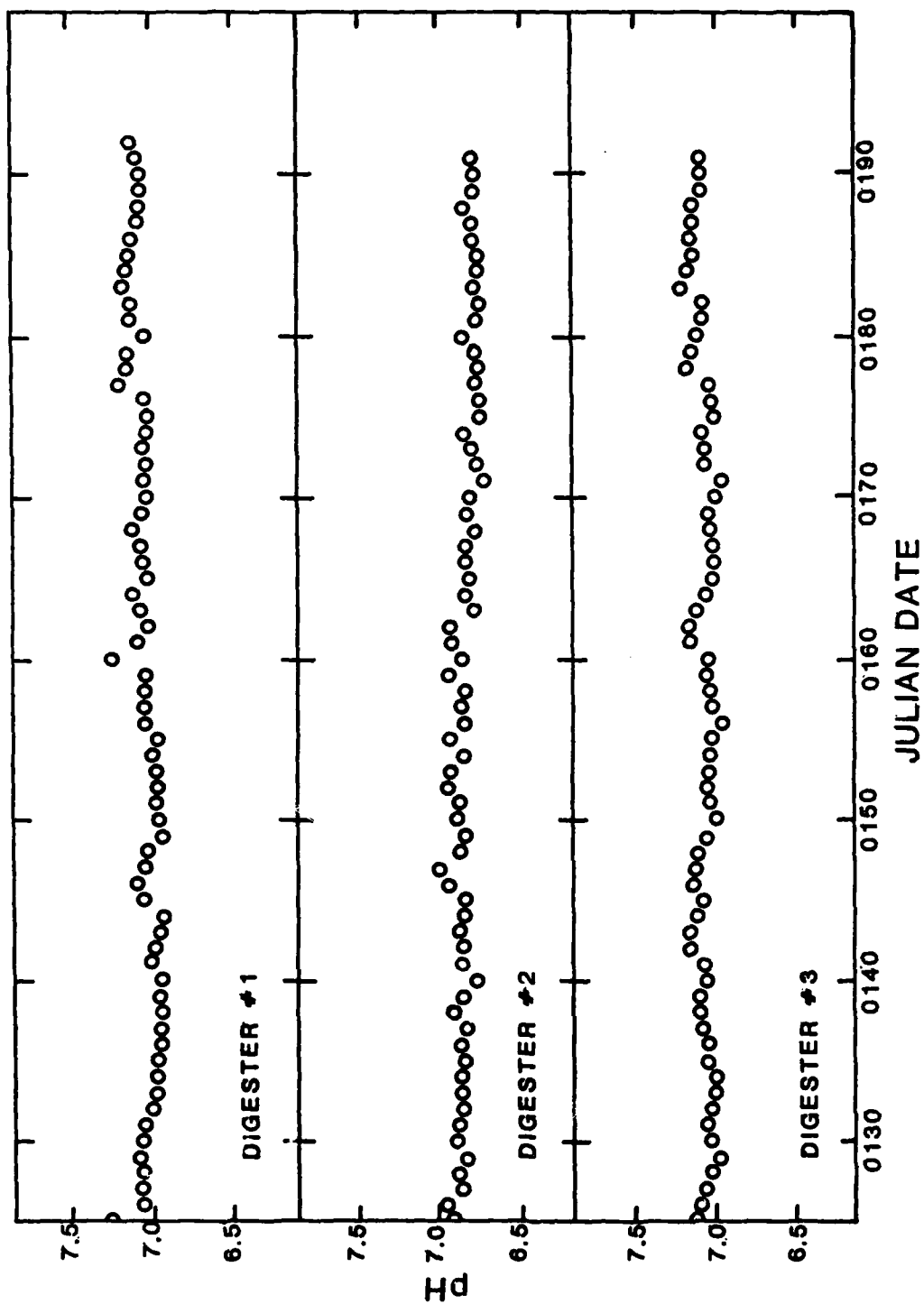


Figure 6. pH Profile for run 3. Commercial grade lime was used to make sludge for digesters 1 and 3. Digester 2 was the control unit.

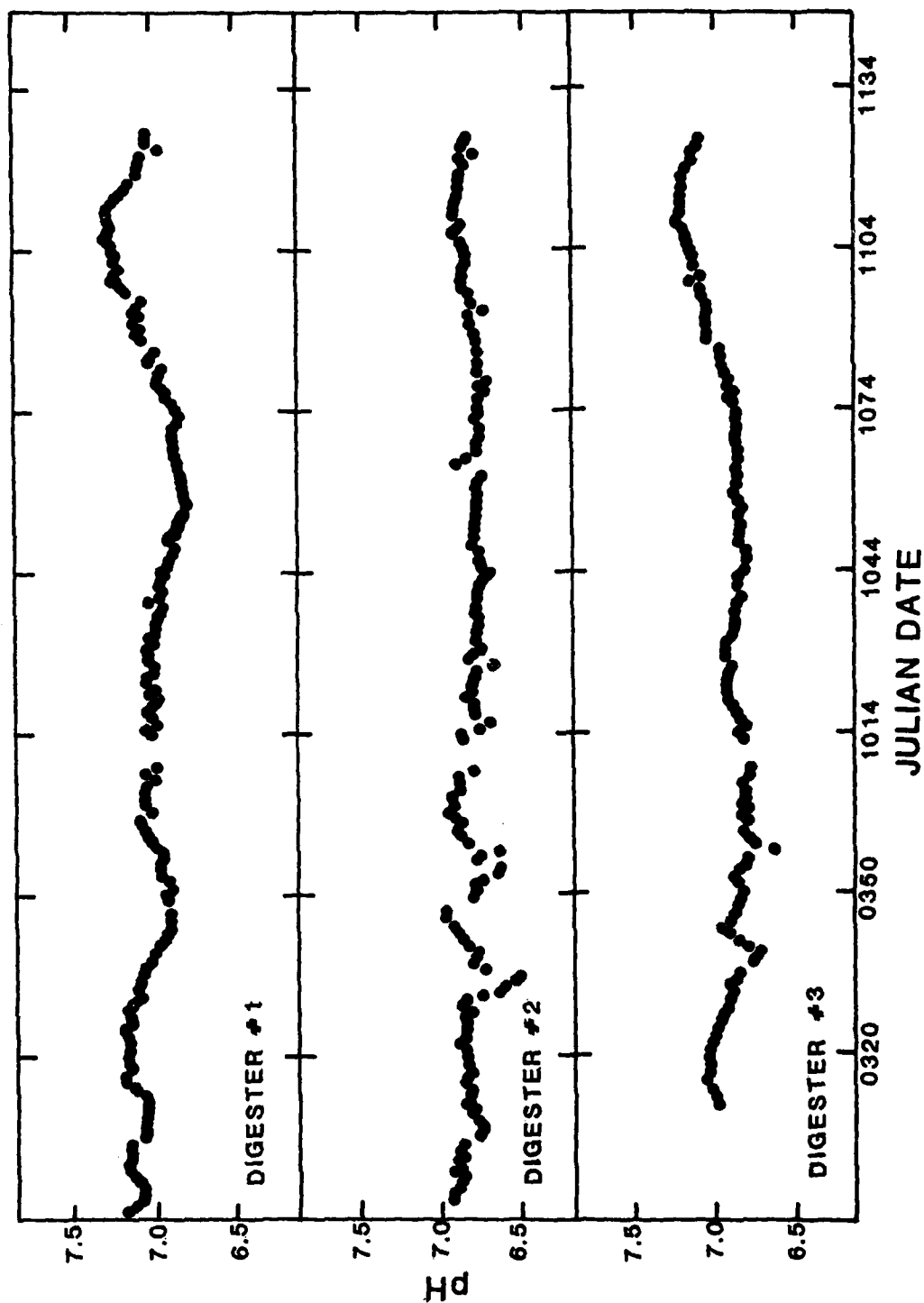


Figure 7. pH Profile for run 4. Commercial grade lime was used to make sludge for digester 1. Digester 2 was the control unit. Reagent grade lime was used to make sludge for digester 3.

TABLE 9. AVERAGE SOLUBLE PHOSPHORUS CONCENTRATIONS

Reactor	Run	Julian Date	Feed PO <sub>4</sub> -P mg/L	Effluent PO <sub>4</sub> -P mg/L
1	1	9309-0008	6.1	7.7
2	1	9309-0008	21.6	12.1
3	1	9309-0008	6.1	7.3
1	2	0050-0099	2.4	9.6
3	2	0050-0099	2.4	8.3
1	3	0125-0199	1.4	8.6
2	3	0125-0191	23.1	10.4
3	3	0125-0190	1.3	9.0
1	4	0291-1126	4.9	15.7
2	4	0294-1126	35.6	22.4
3	4	0312-1126	7.2	12.6

TABLE 10. AVERAGE AMMONIA NITROGEN CONCENTRATIONS

Reactor	Run	Julian Date	Feed NH <sub>3</sub> -N mg/L	Effluent NH <sub>3</sub> -N mg/L
1	1	9261-9313	100	203
1	1	9314-0008	58	243
2	1	9261-0008	72	147
3	1	9261-9313	90	157
3	1	9314-0008	58	183
1	2	0050-0099	62	237
3	2	0050-0099	63	225
1	3	0125-0199	37	131
2	3	0125-0191	42	126
3	3	0125-0190	37	132
1	4	0291-1126	132	267
2	4	0294-1126	102	325
3	4	0312-1126	118	221

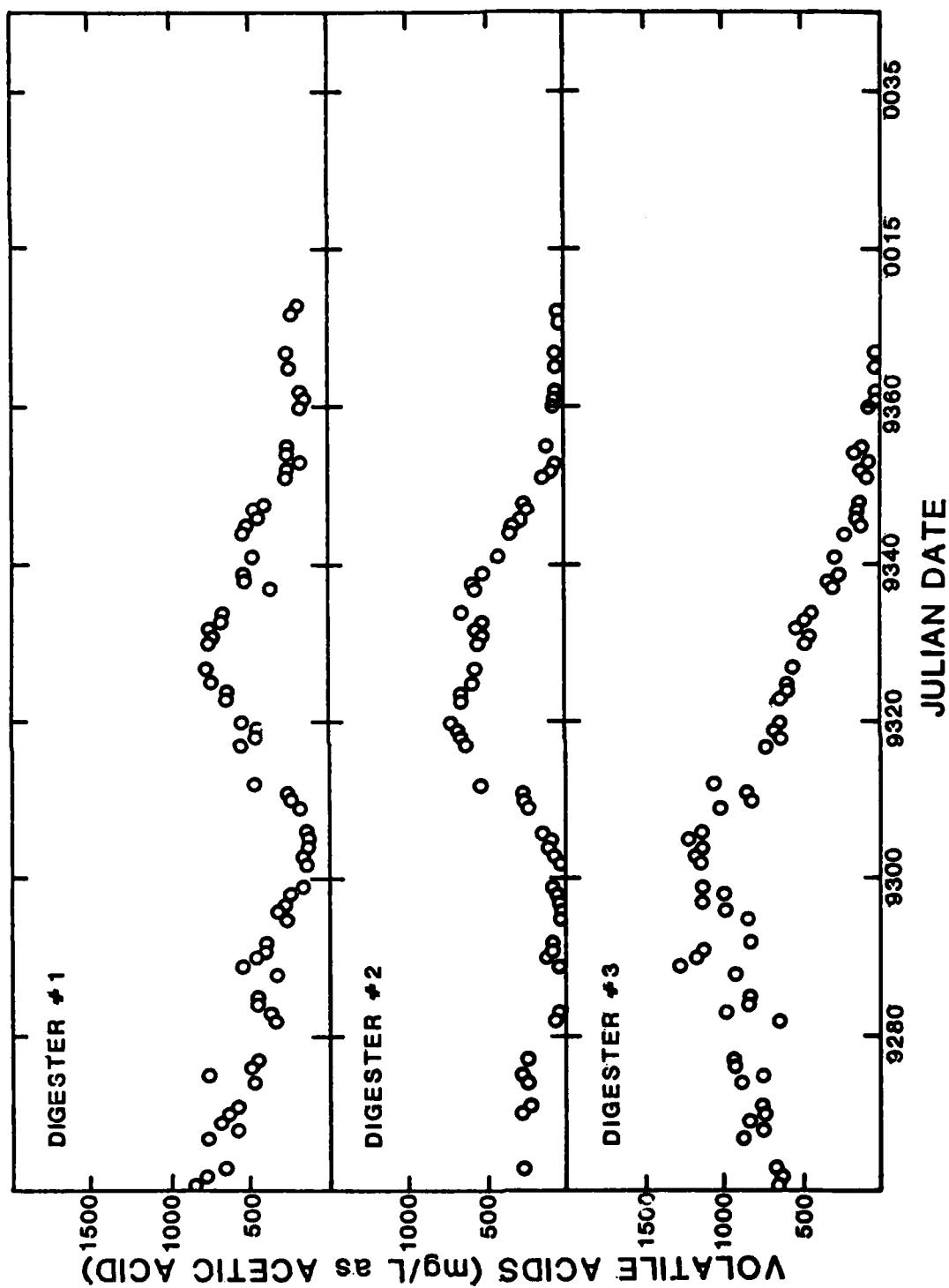


Figure 8. Volatile acids profile for run 1. Commercial grade lime was used to make sludge for digesters 1 and 3. Digester 2 was the control unit.



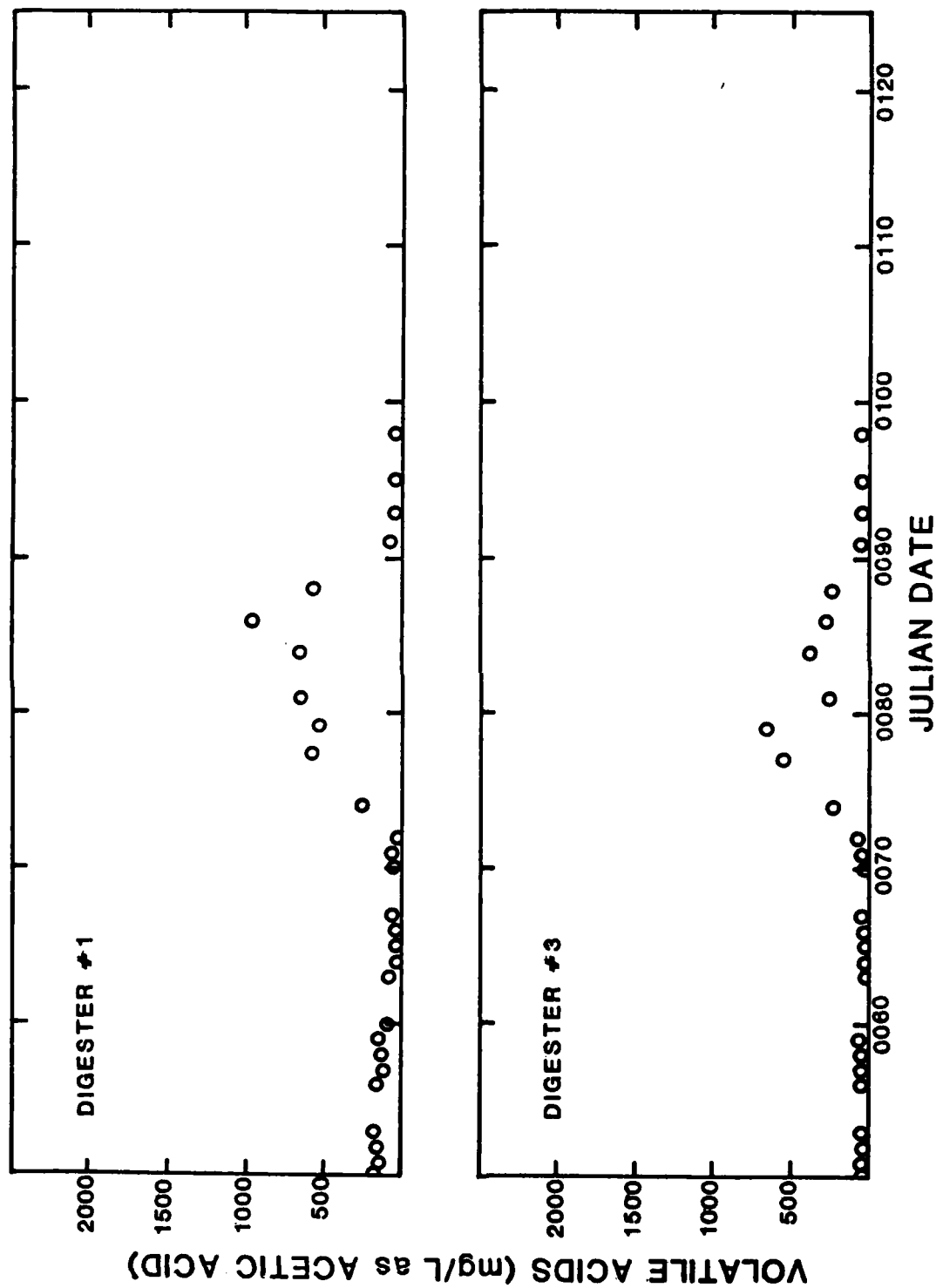


Figure 9. Volatile acids profile for run 2. Commercial grade lime was used to make sludge for digesters 1 and 3.

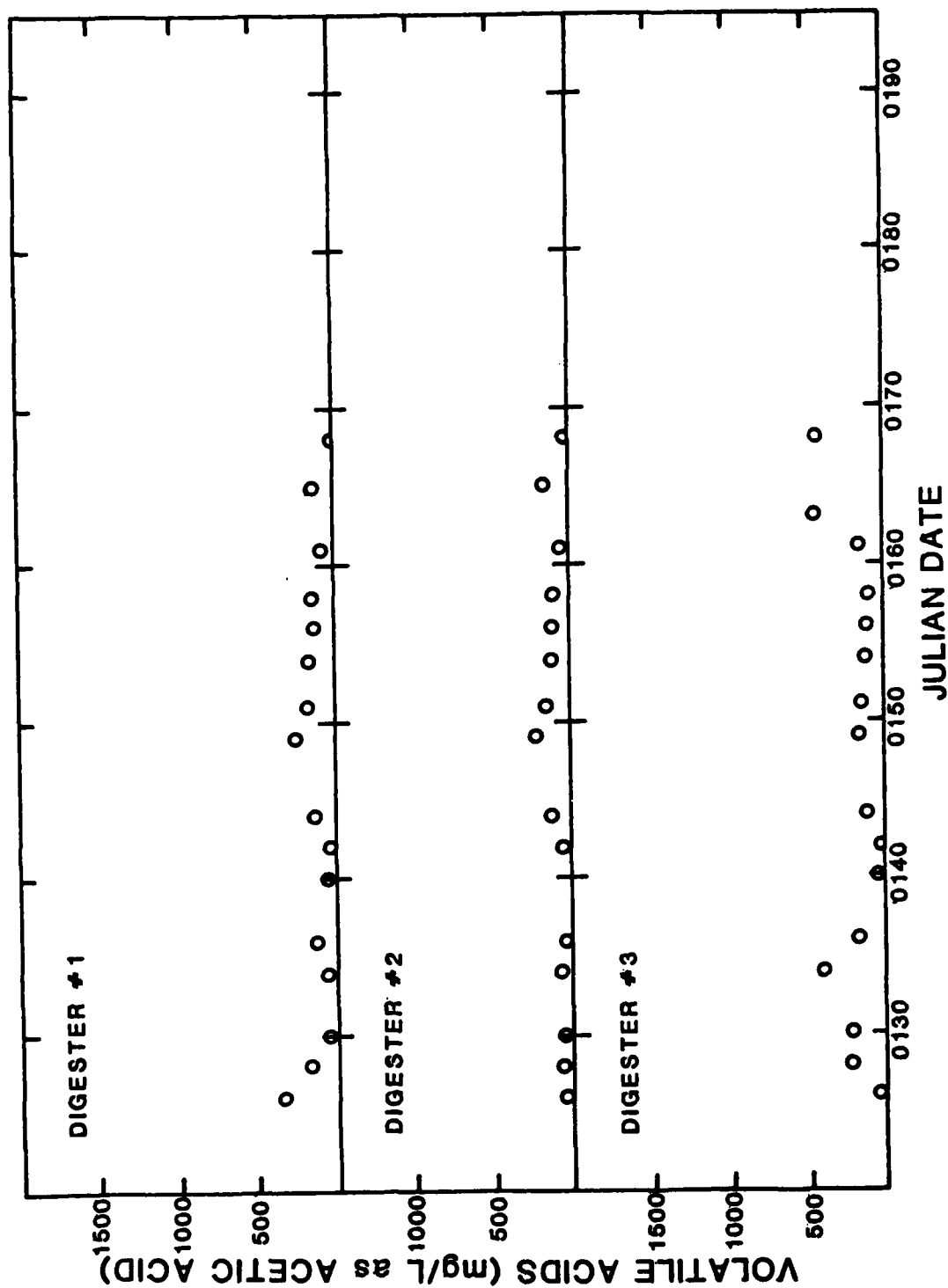


Figure 10. Volatile acids profile for run 3. Commercial grade lime was used to make sludge for digesters 1 and 3. Digester 2 was the control unit.

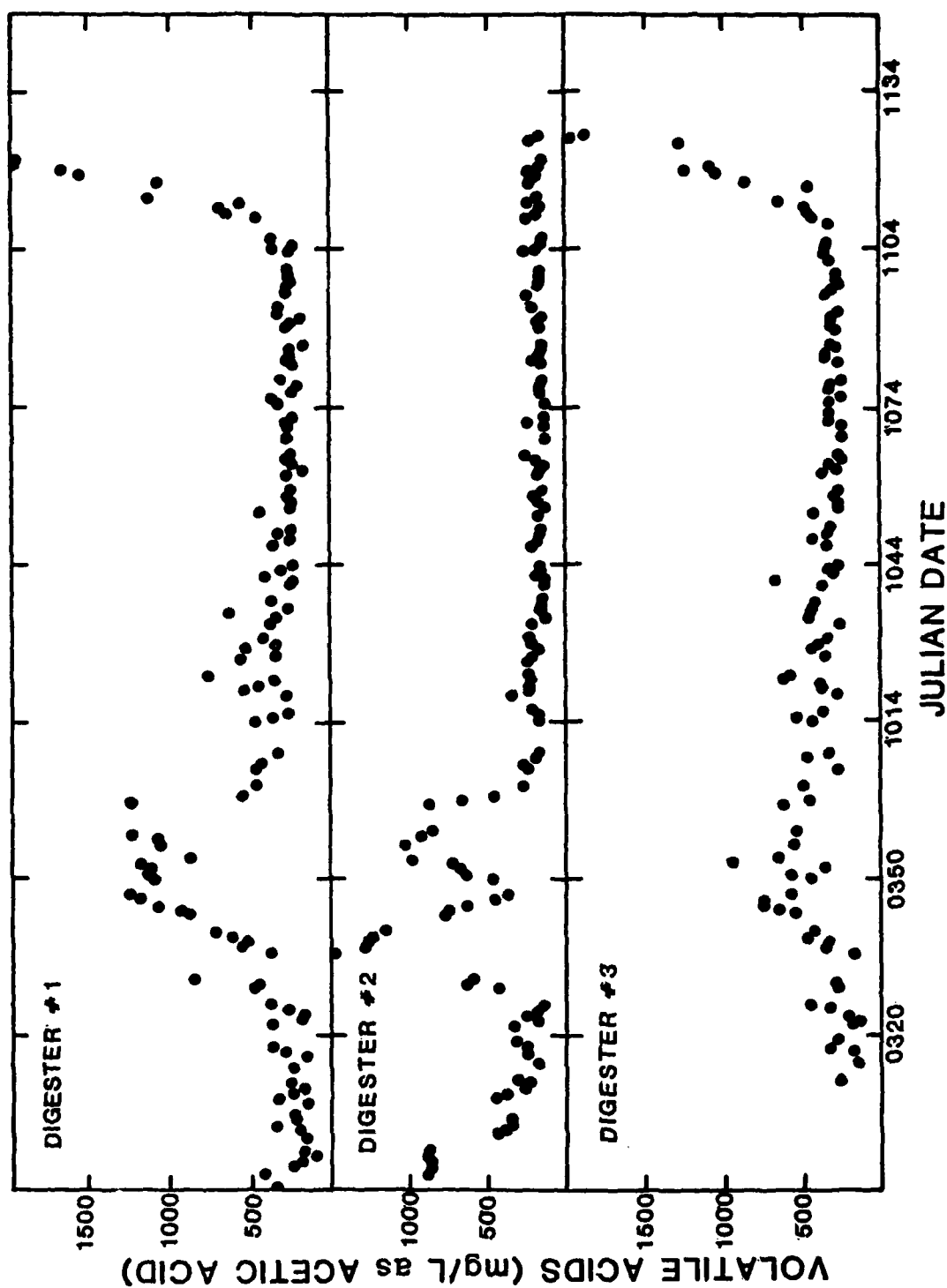


Figure 11. Volatile acids profile for run 4. Commercial grade lime was used to make sludge for digester 1. Digester 2 served as the control unit. Reagent grade lime was used to make sludge for digester 3.

## GAS PRODUCTION

Gas production was measured daily. Due to temperature and barometric pressure changes the gas production was calculated as L/day at standard temperature (0°C) and standard pressure (1 ATM). The gas productions for the reactors are presented in Figures 12 through 22.

Gas composition was monitored qualitatively on runs 1 and 2 by igniting the gas. This was merely a check for the presence of methane. Gas analysis was carried out on the latter portion of run 3 (0170-0199), by utilizing an Orsat® gas analyzer. The gas from the control digester averaged 26.5 percent CO<sub>2</sub> and approximately 73.5 percent CH<sub>4</sub>. The gas from the two lime sludge digesters averaged approximately 15.5 percent CO<sub>2</sub> and 84.5 percent CH<sub>4</sub>. These values are in the range normally expected for primary sludge<sup>9</sup> and lime sludge<sup>26</sup> digestion. During run 4, the gas quality was measured, and the average CO<sub>2</sub> percentage is presented in Table 11. The daily methane production is shown for run 4 in Figures 20 through 22.

TABLE 11. AVERAGE CO<sub>2</sub> GAS COMPOSITION  
DURING RUN 4

Reactor	% CO <sub>2</sub>		
	Average	High	Low
1	17	24	12
2	28	40.5	17.5
3	18	23.5	11.5

The analytical results obtained using the Orsat Analyzer® were confirmed by periodic gas analyses by gas chromatography. Good agreement was found between the Orsat and chromatographic analyses.

## HEAVY METALS

The concentration of heavy metals was first measured at the end of run 3 (Table 12). During run 4, monthly heavy metal scans were performed, and Table 13 presents the average concentrations. Both total and soluble concentrations were determined.

## ALKALINITY

The total alkalinity was measured daily in the reactor effluents. The average alkalinity during each run is shown in Figure 23. Since alkalinity in this system primarily results from Ca(OH)<sub>2</sub> addition and is in the form of Ca(HCO<sub>3</sub>)<sub>2</sub>, a linear relationship would be expected between calcium ion concentration and the total alkalinity. This relationship is shown in Figure 24 for run 4.

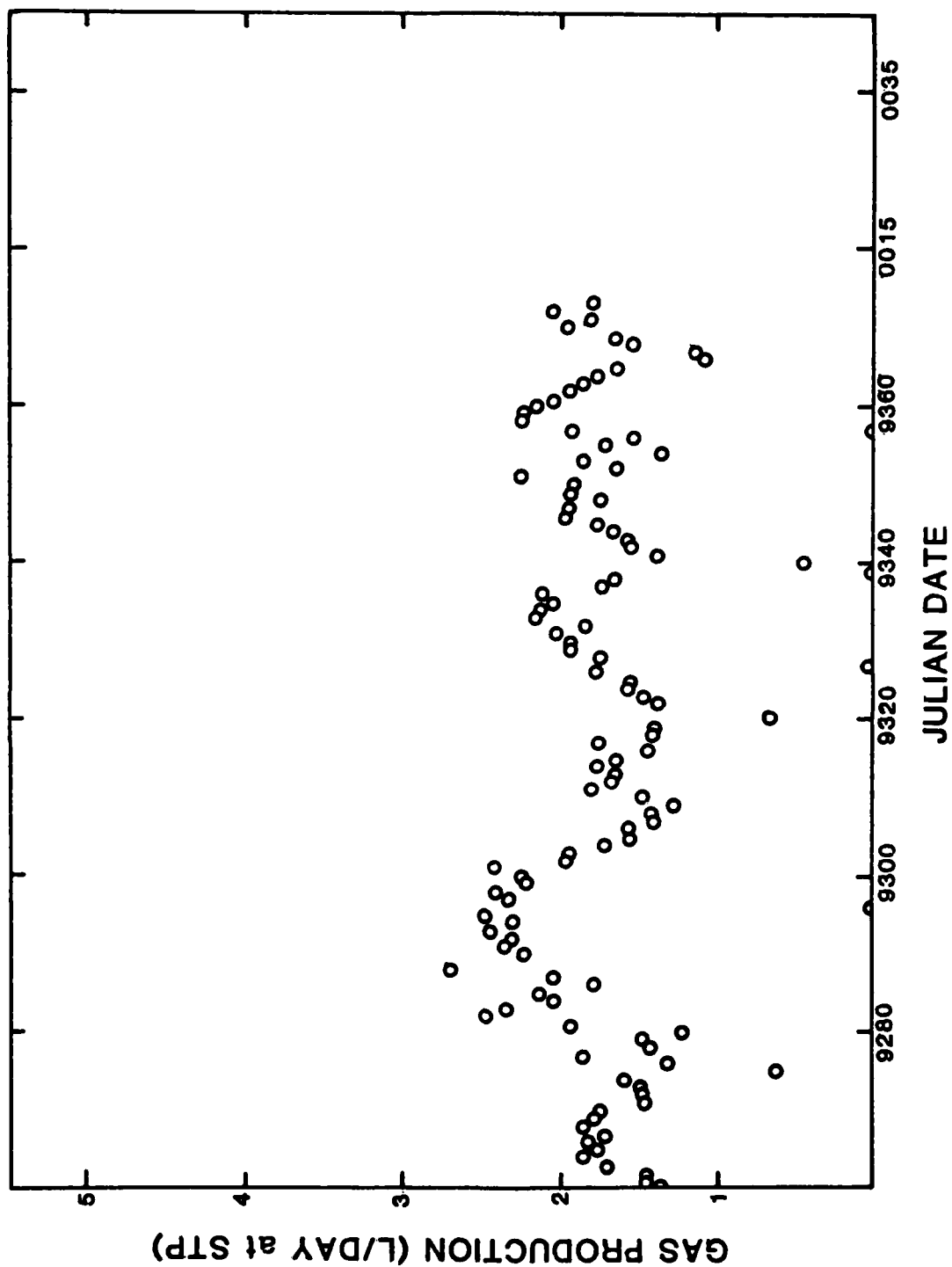


Figure 12. Daily gas production for digester 1, run 1 (commercial grade lime).

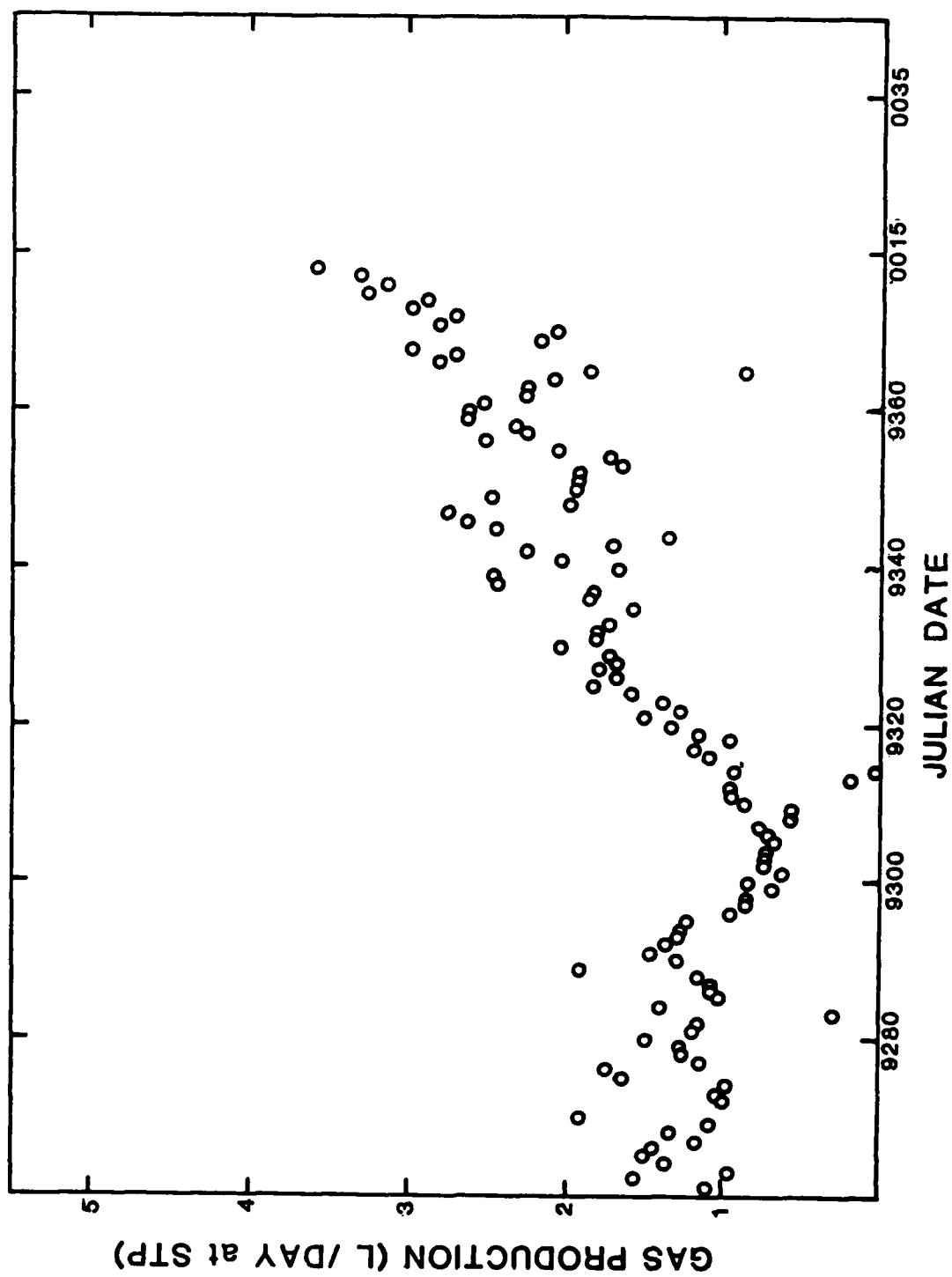


Figure 13. Daily gas production for digester 2, run 1 (control).

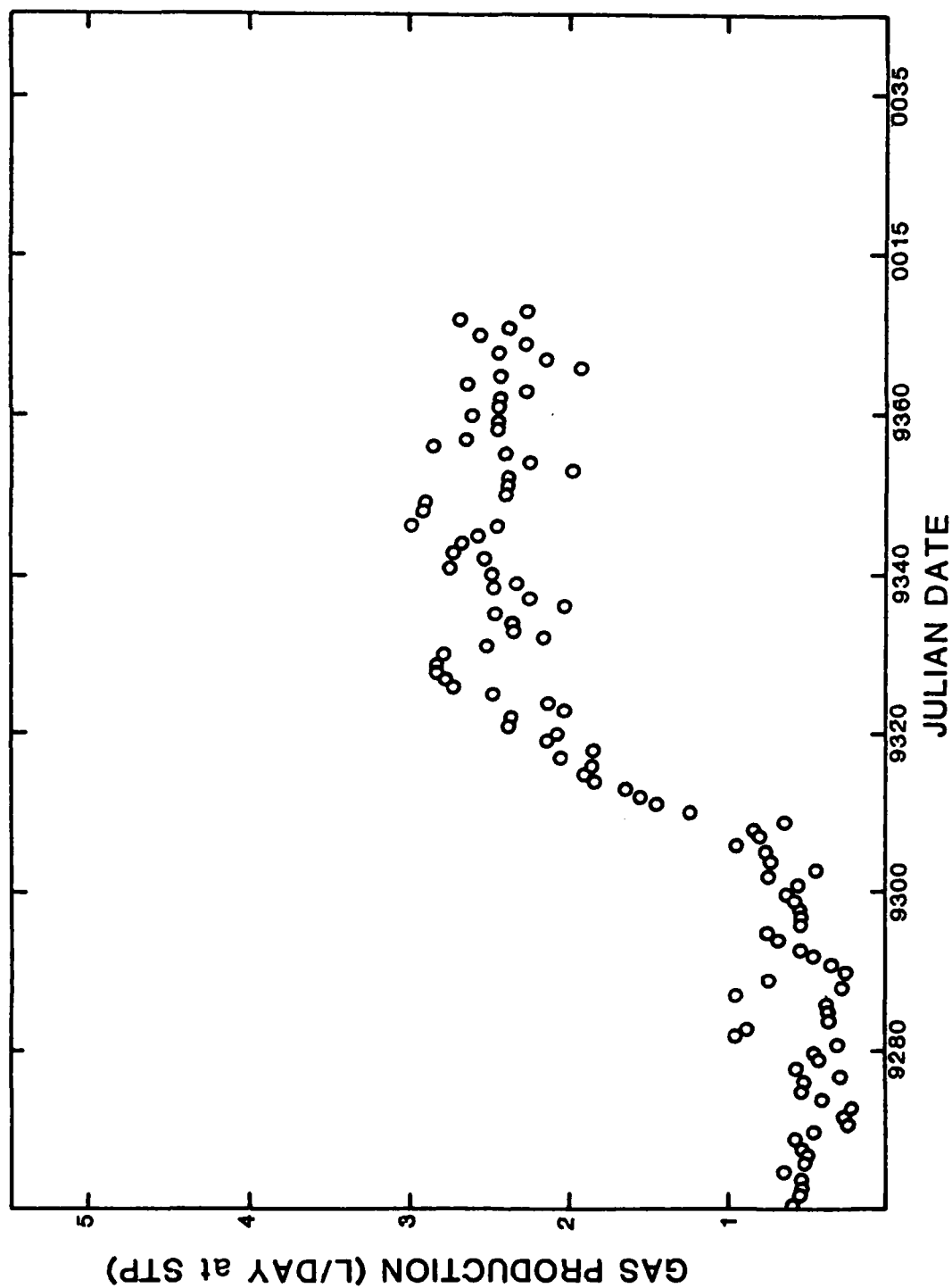


Figure 14. Daily gas production for digester 3, run 1 (commercial grade lime).

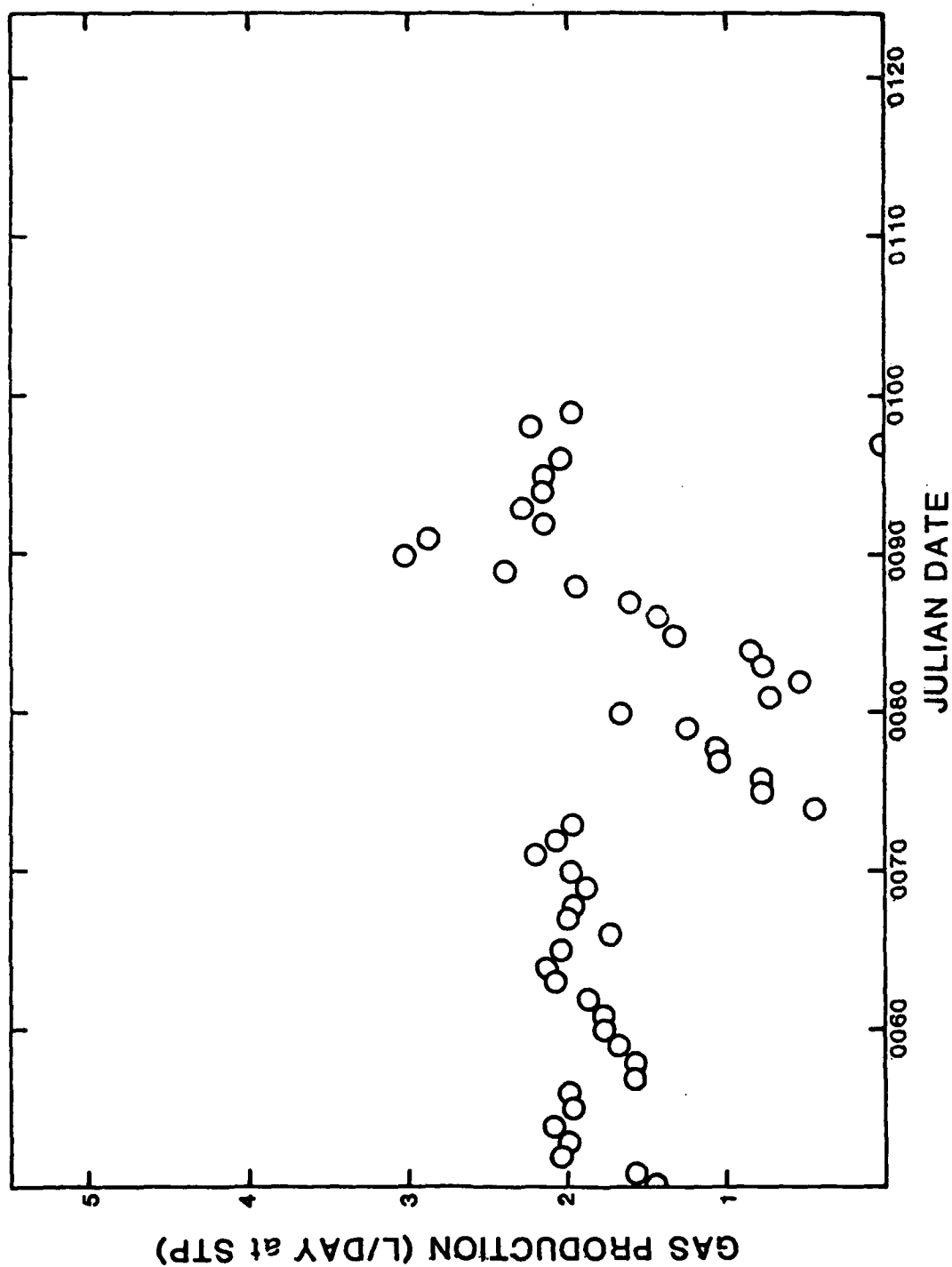


Figure 15. Daily gas production for digester 1, run 1 (commercial grade lime).



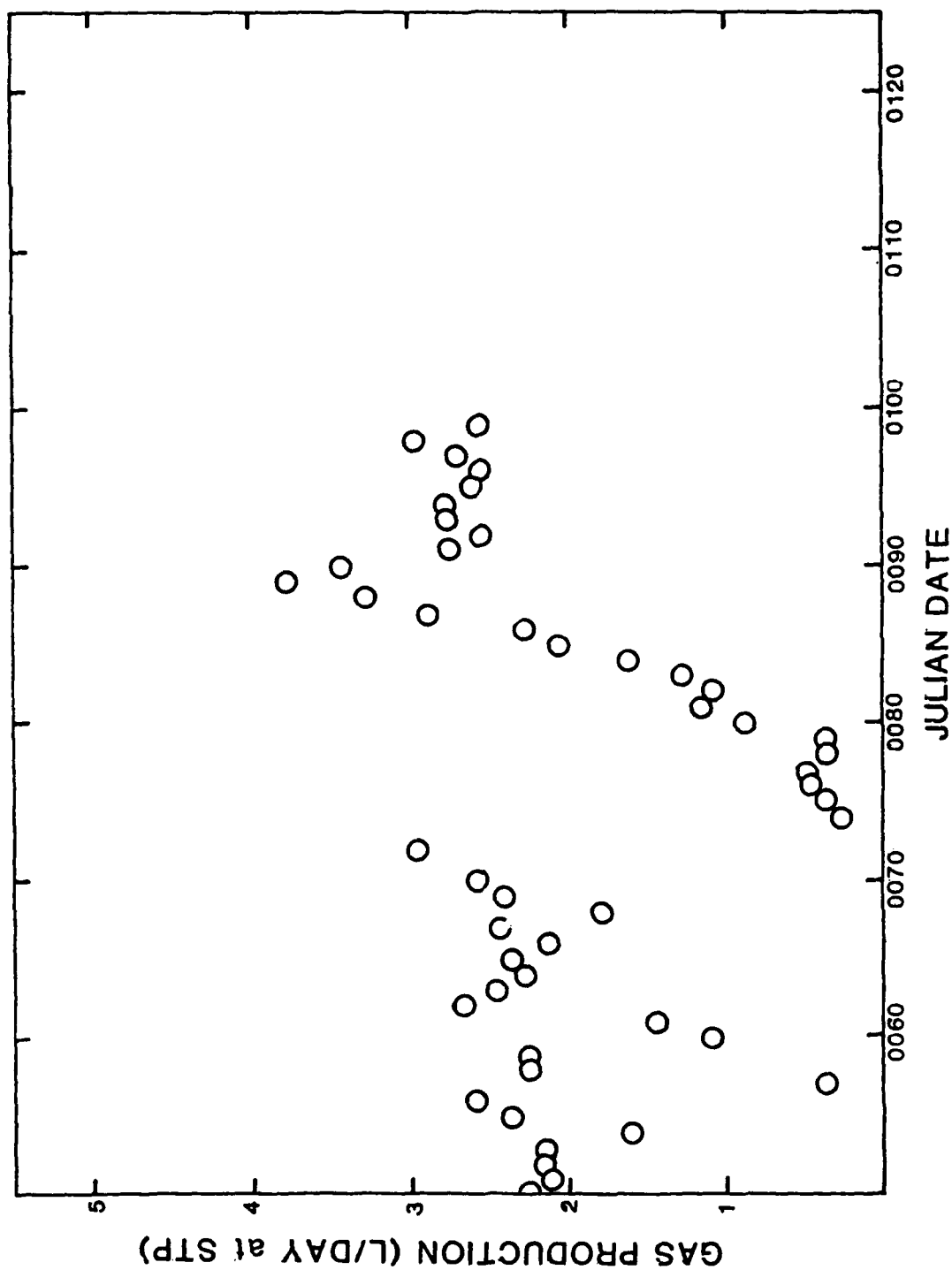


Figure 16. Daily gas production for digester 3, run 2 (commercial grade lime).

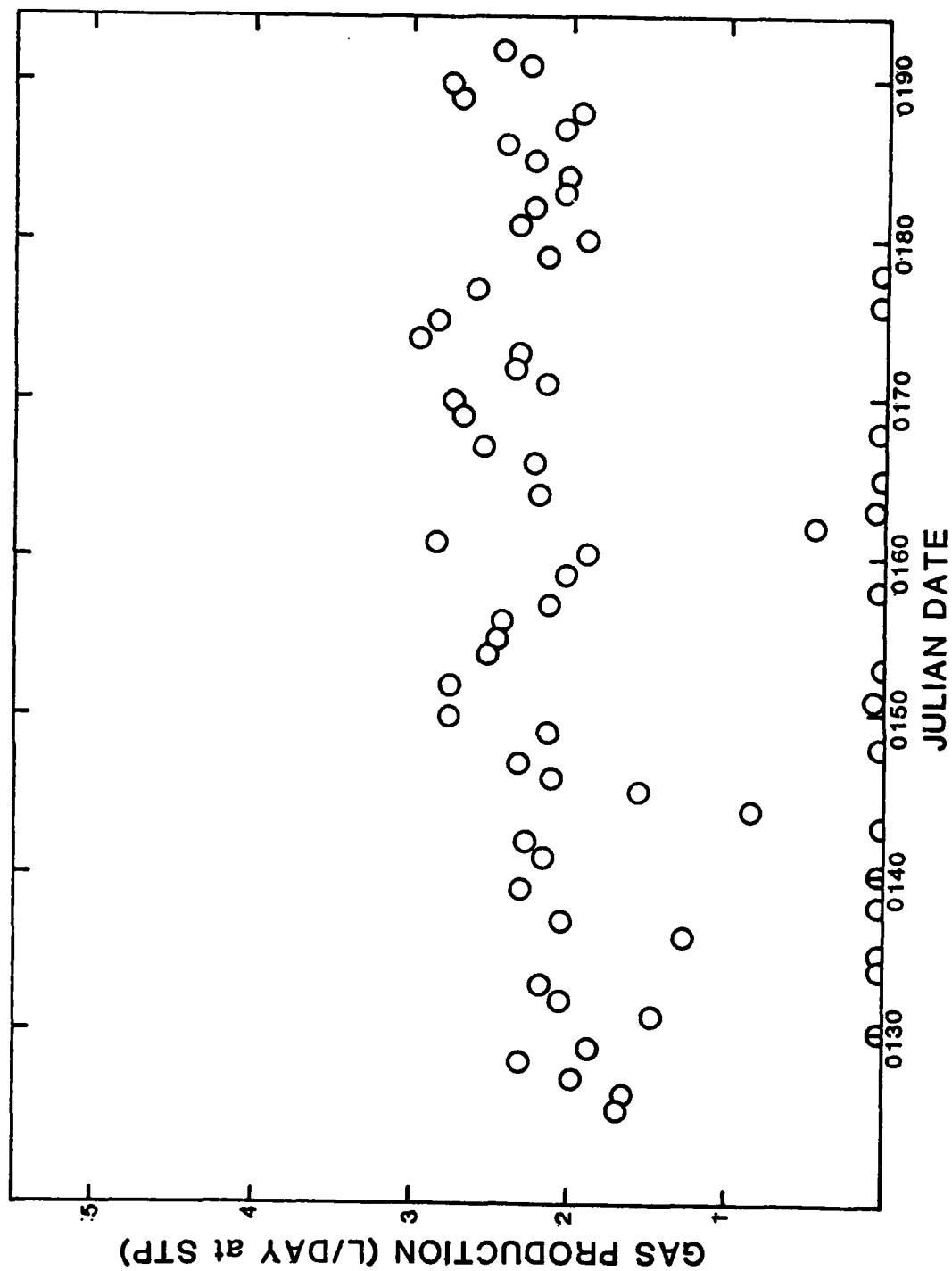


Figure 17. Daily gas production for digester 1, run 3 (commercial grade lime).

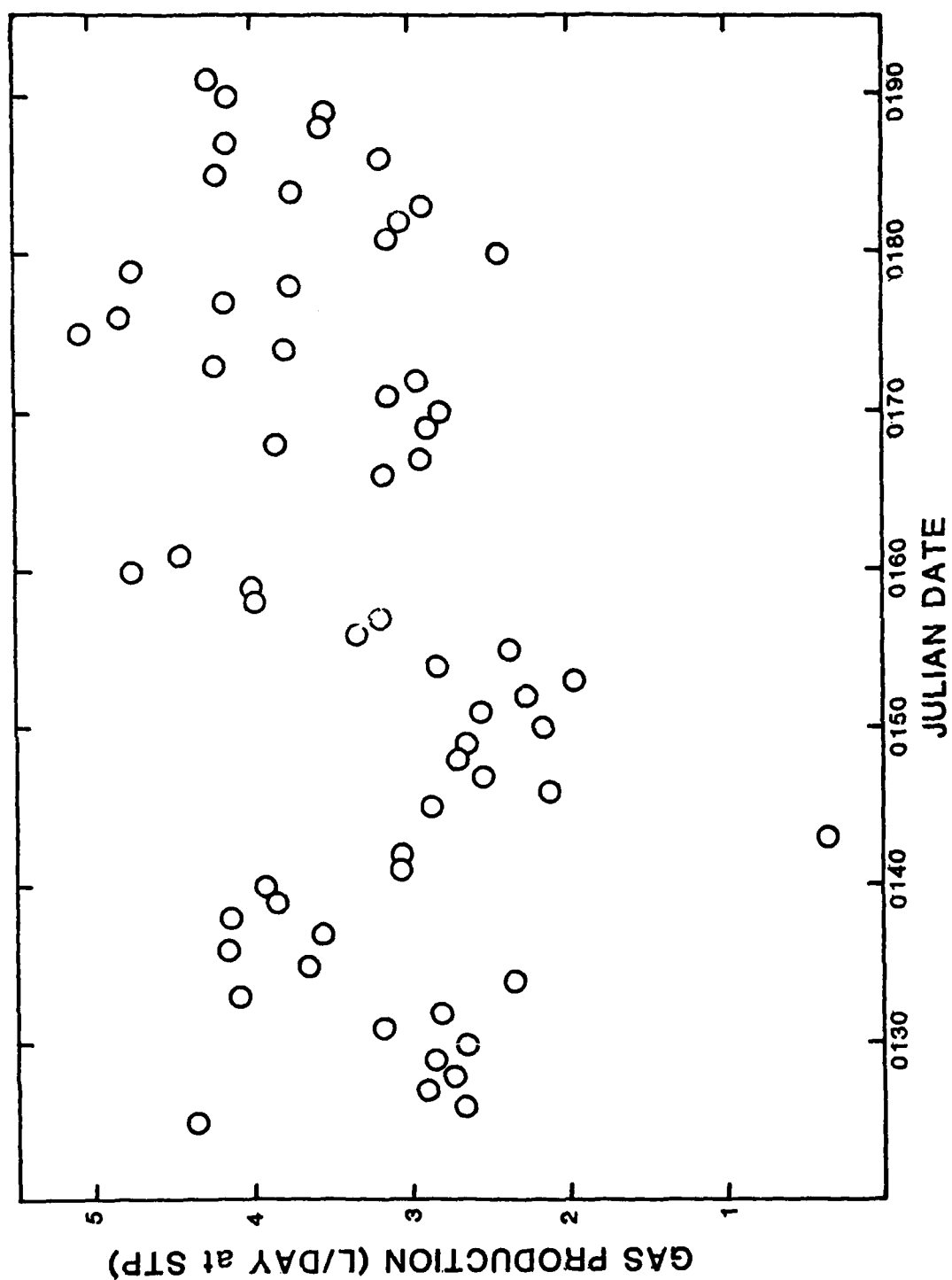


Figure 18. Daily gas production for digester 2, run 3 (control).

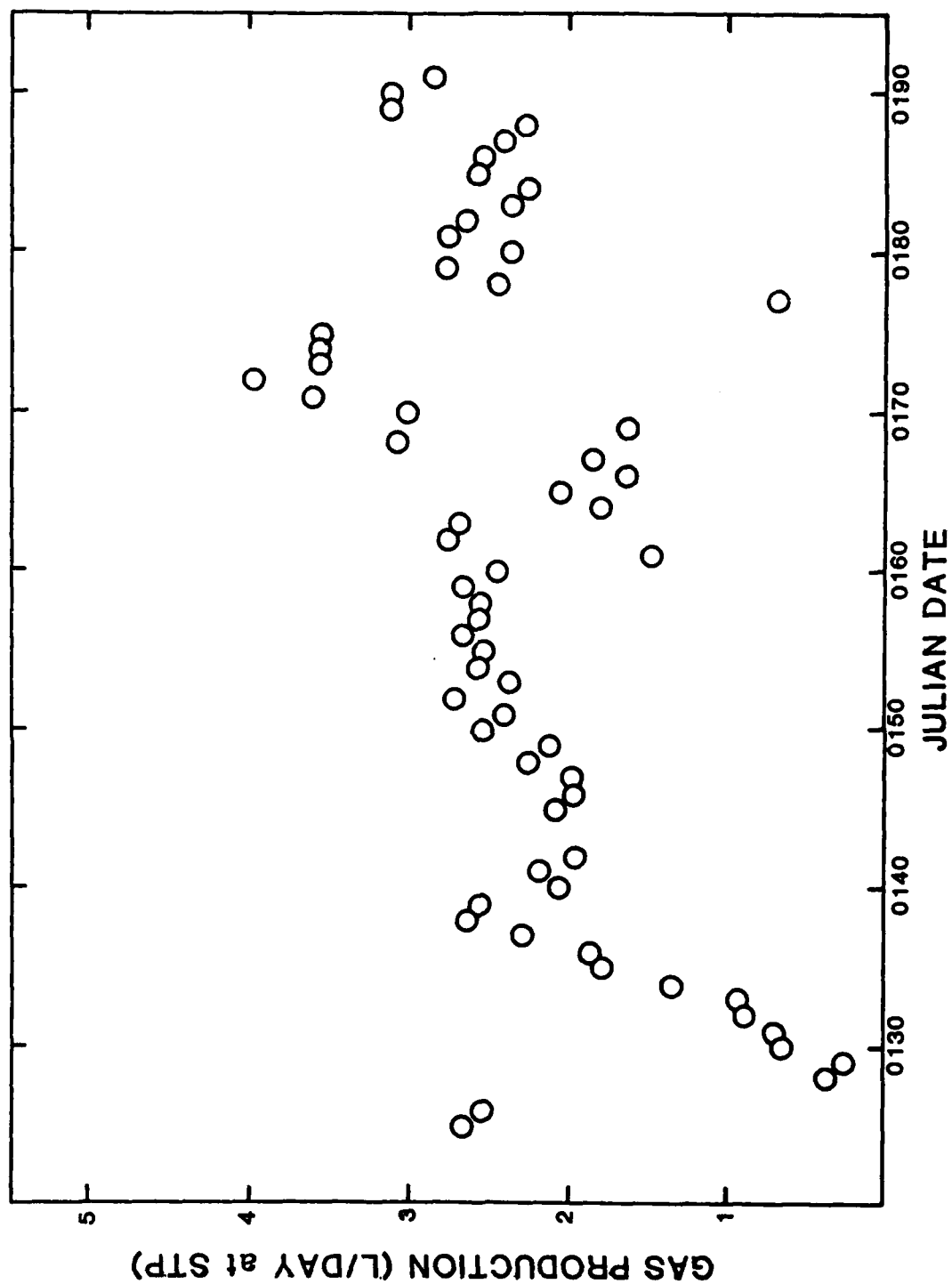


Figure 19. Daily gas production for digester 3, run 3 (commercial grade lime).

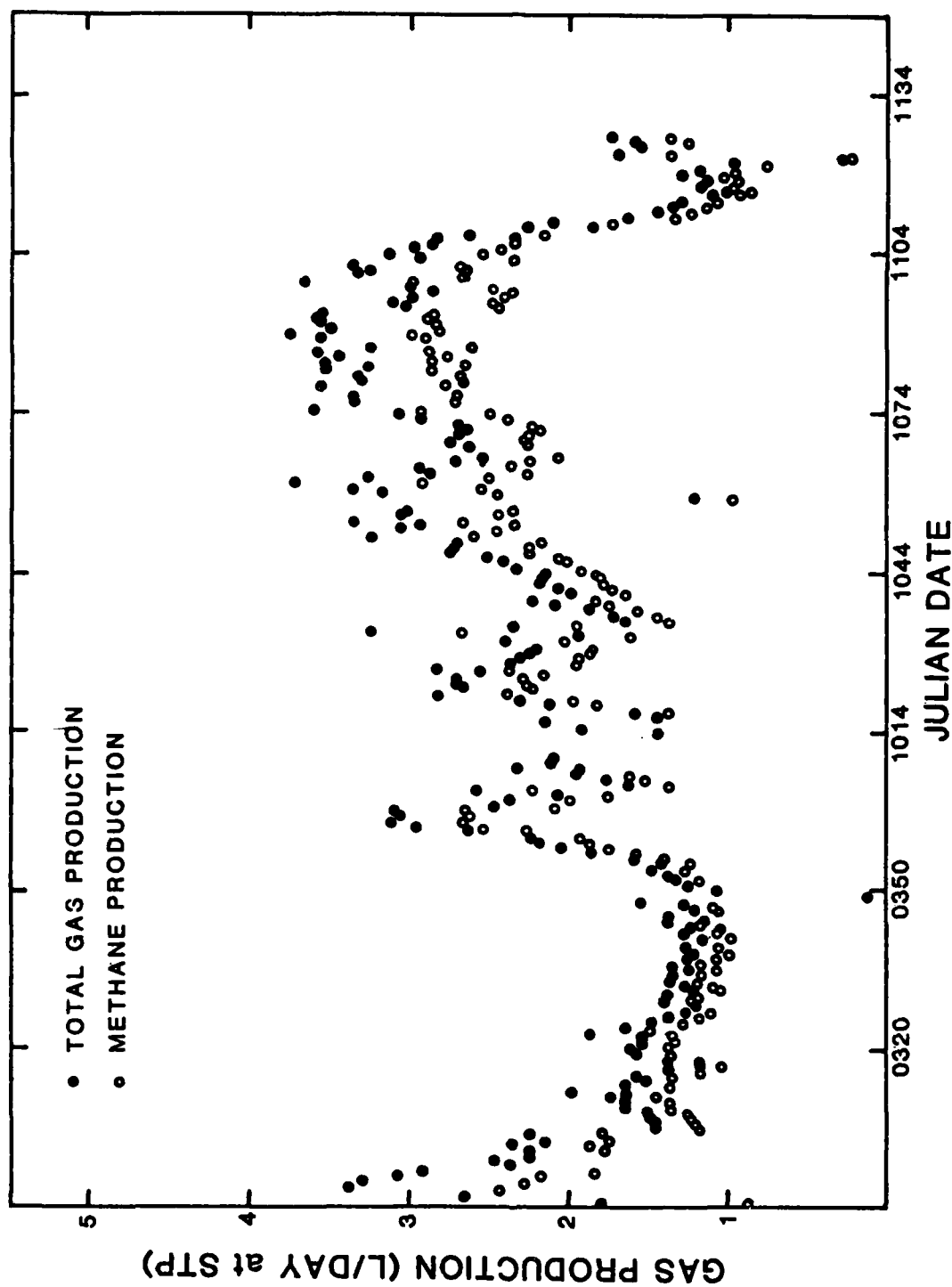


Figure 20. Daily gas production for digester 1, run 4 (commercial grade lime).

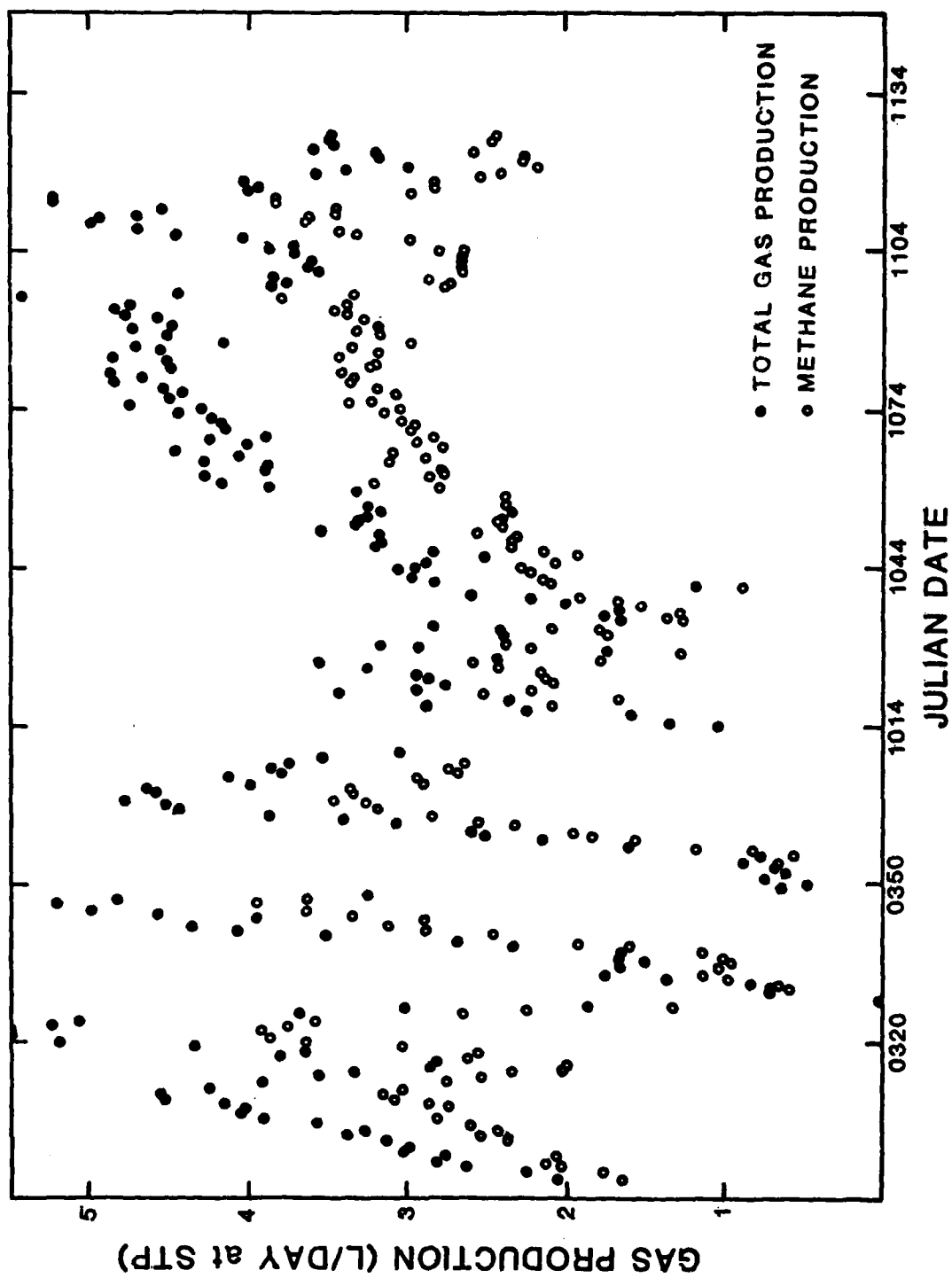


Figure 21. Daily gas production for digester 2, run 4 (control).

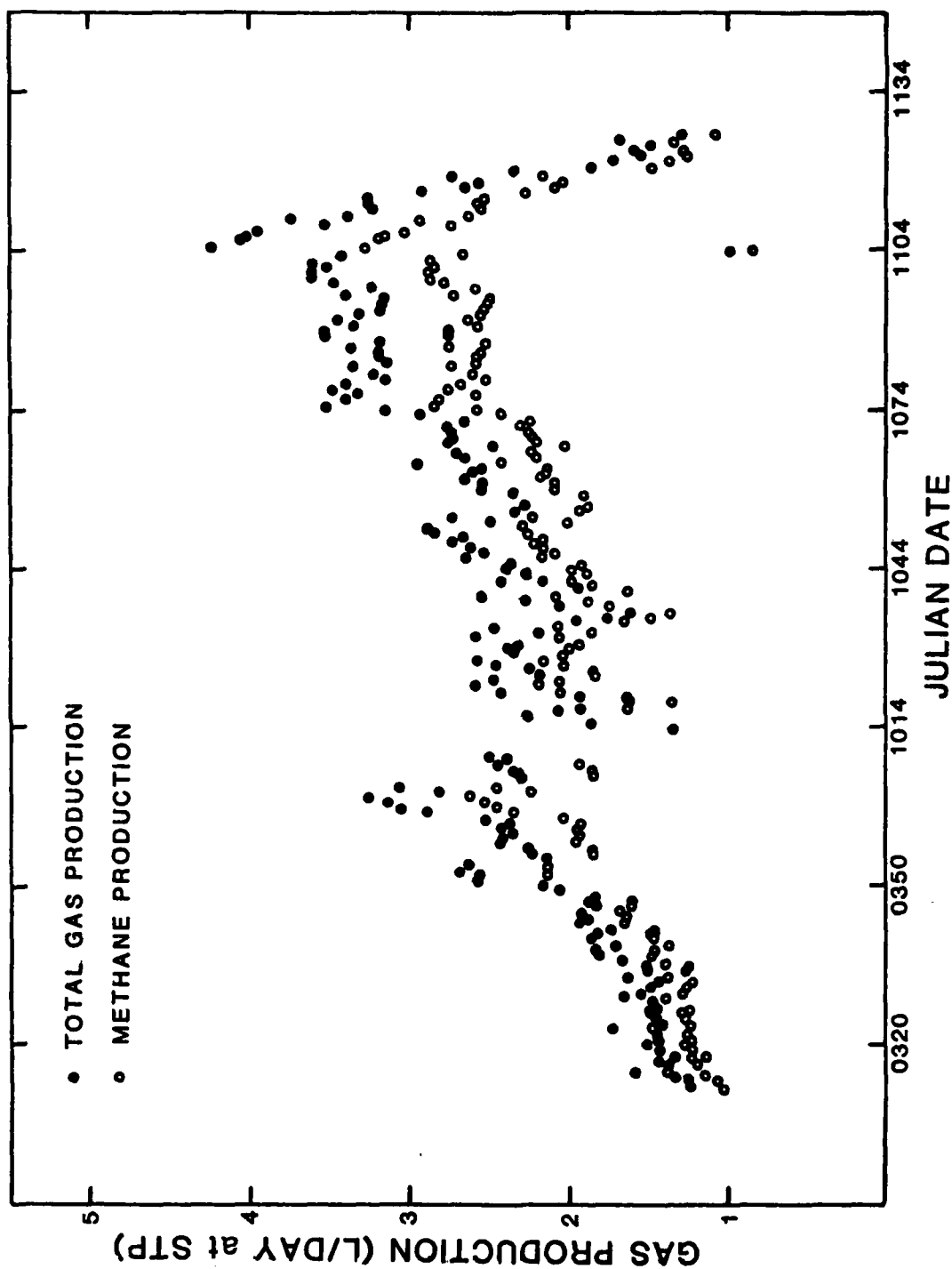


Figure 22. Daily gas production for digester 3, run 4 (reagent grade lime).

TABLE 12. HEAVY METALS IN DIGESTER EFFLUENTS  
AT THE END OF RUN 3

Heavy Metal	Control (mg/L)		Lime Digester (mg/L)	
	Total	Soluble	Total	Soluble
Zinc	31.7	<1.0	44.4	<1.0
Nickel	12.4	<1.0	9.8	<1.0
Iron	329.0	<1.0	371.0	<1.0
Cadmium	--	--	--	--
Chromium	12.8	<1.0	9.0	<1.0
Copper	9.4	<1.0	9.4	<1.0
Lead	4.0	<1.0	5.1	<1.0

TABLE 13. AVERAGE HEAVY METAL CONCENTRATIONS IN DIGESTER EFFLUENTS  
DURING RUN 4

Heavy Metal	Digester 1 (mg/L)		Digester 2 (mg/L)		Digester 3 (mg/L)	
	Total	Soluble	Total	Soluble	Total	Soluble
Zinc	13.5	<0.1	10.0	<0.1	13.3	<0.1
Nickel	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Iron	143.2	<1.0	128.0	<1.0	123.3	<1.0
Cadmium	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chromium	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Copper	8.0	<0.2	7.0	<0.2	8.6	<0.2
Lead	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0



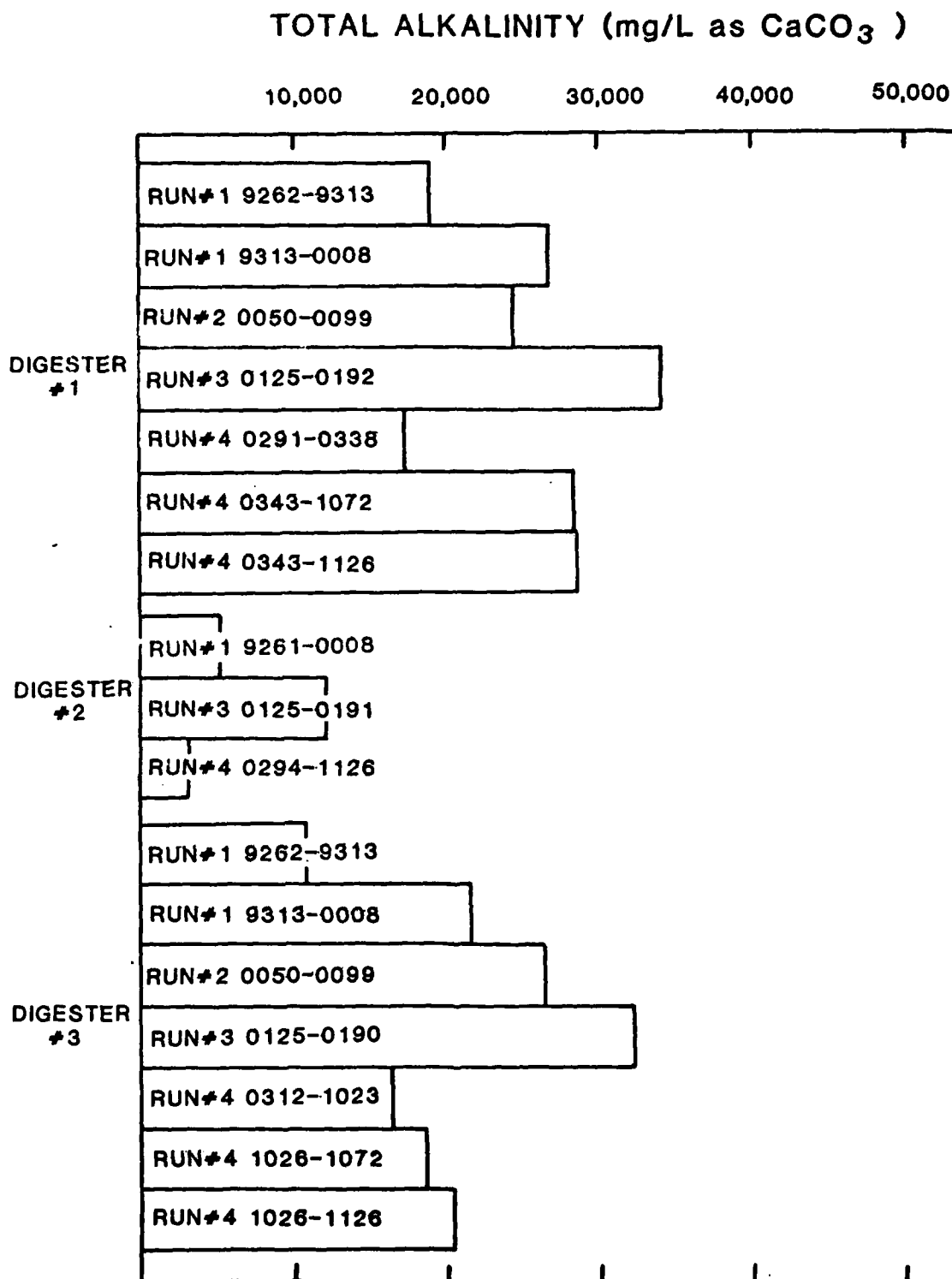


Figure 23. Average total alkalinity for each digester. Commercial grade lime was used to make sludge for digester 1, all runs, and for digester 3, runs 1 through 3. Digester 2 served as the control unit. Reagent grade lime was used to make sludge for digester 3, run 4.

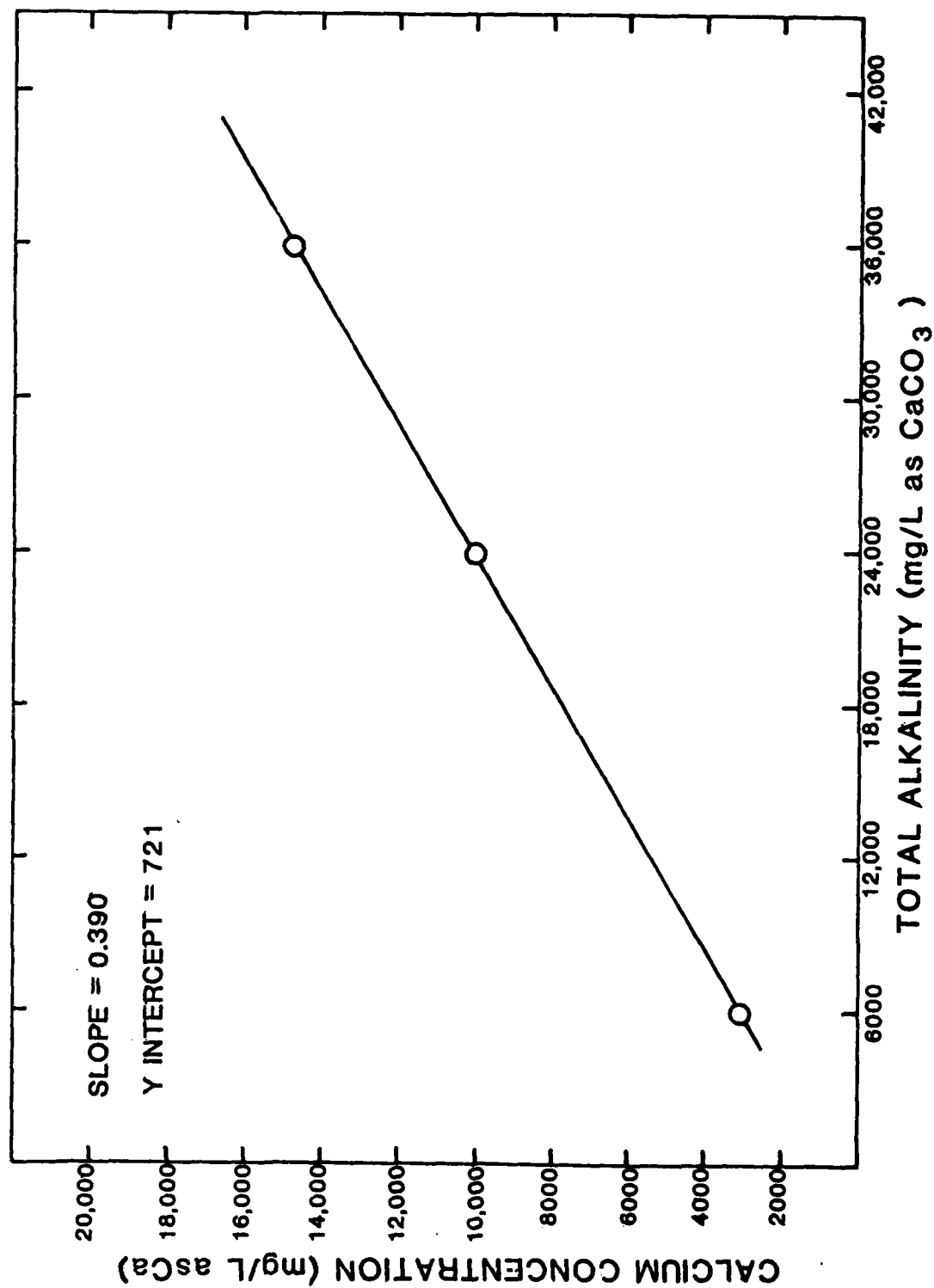


Figure 24. Calcium concentration vs. alkalinity for digesters 1 through 3, run 4.

## LIGHT METAL CATIONS

A scan for the light metal cations was done at least once per week during run 4. The profiles of the light metal cations for each digester are shown for potassium, sodium, magnesium, and calcium in Figures 25 through 28, respectively. Potassium was not added to any of the digesters, and the potassium concentration dropped to a steady-state value throughout the last 100 days of run 4 (Fig. 25). Sodium additions to digesters 1 and 3 began on Julian date 1075 and continued until the end of run 4 (Fig. 26). Two different grades of lime were used during run 4. Digester 1 received commercial grade lime, whereas digester 3 received reagent grade lime. Consequently, different magnesium levels were found, as shown in Figure 27. The differences between the two types of lime can also be seen in the calcium levels, as shown in Figure 28.

Calcium concentrations for each reactor were calculated from alkalinity data (Fig. 24) for runs 1 to 3 and are presented with calcium data from run 4 in Figure 29.

## VOLATILE SOLIDS DESTRUCTION

Figures 30 through 34 show volatile solids destruction as a function of volatile solids applied for all digesters and runs. The relationships in all cases are linear. A least squares analysis was performed on the data. The results of the least squares analysis are presented in Table 14. A comparison of parameters from the best fits to the data using the analysis of variance technique to test for differences in slopes and differences in intercepts was performed on all the runs. A shift in the destroyed volatile solids versus applied volatile solids was present at about 8,000 mg/L Ca. Therefore, 8,000 mg/L Ca was used as the transition concentration between high and low lime levels. Because there was so little scatter in the data, a 95 percent confidence interval had to be imposed on the statistical comparison in order to obtain meaningful results. The results of the comparison of slopes and intercepts are shown in Table 15. Table 16 presents a statistical analysis of slope and intercept comparisons for run 4. The least squares composite lines are presented in Table 17. Both the slopes and intercepts must show no significant difference for the lines to be considered the same. If the slopes are different, the test for the intercepts does not apply.

## COD

The relationship between COD destroyed and COD applied is shown in Figure 35. A least squares analysis and statistical slope and intercept comparisons were done as for the volatile solids (Tables 18 and 19, respectively).

Methane production as a function of COD applied is presented in Figure 36. Equations of the three lines of best fit from Figure 36 are presented in Table 20. Due to scatter in the COD data, weekly averages for COD and gas production were used in preparing Figure 36 and Table 20.

Figure 37 shows a plot of methane produced per gram COD applied versus total alkalinity. Once again weekly averages were used. Table 21 shows the least squares analysis for each reactor and a composite line for all the data.

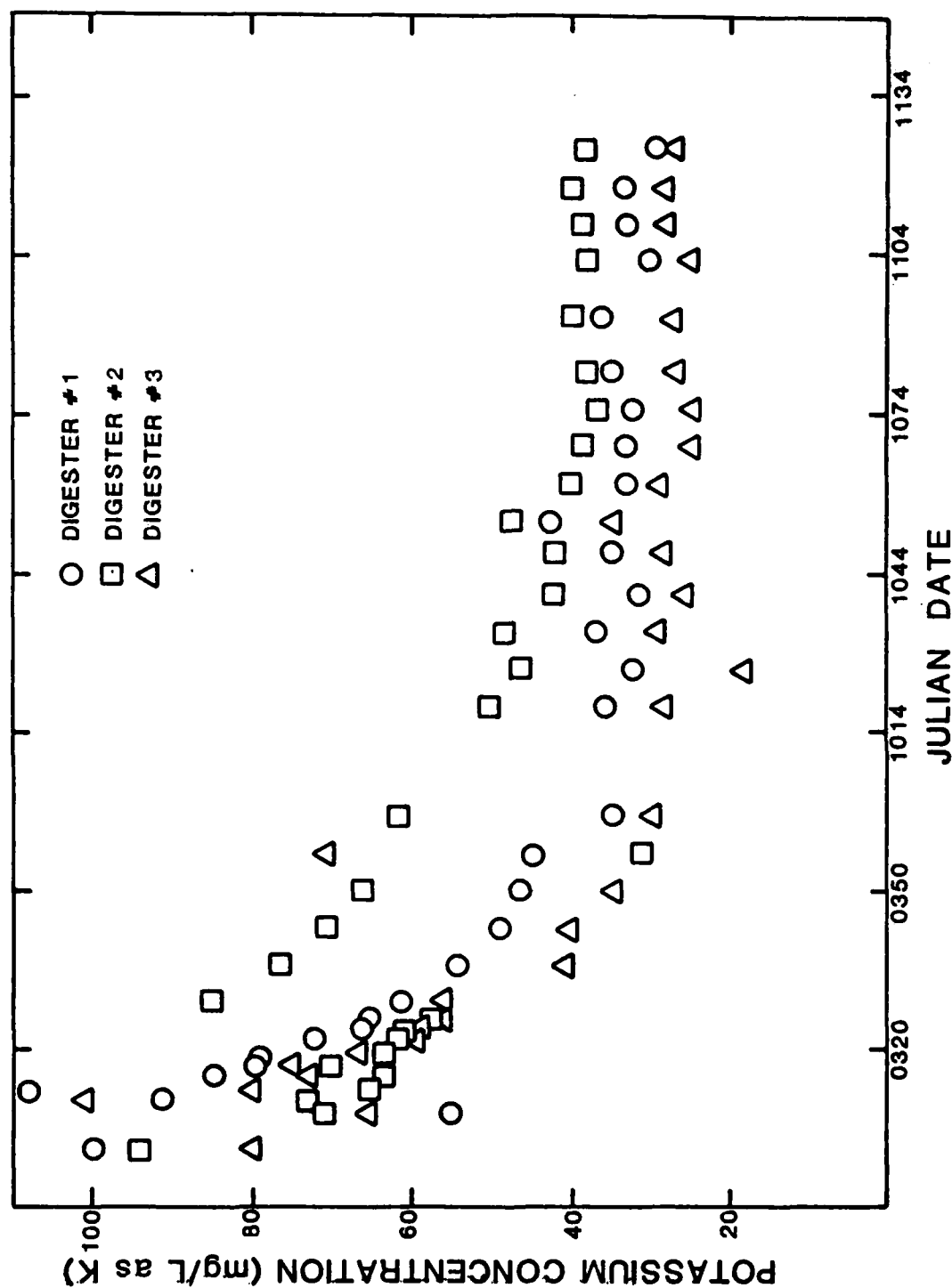


Figure 25. Potassium profiles during run 4. Commercial grade lime was used to make sludge for digester 1. Digester 2 served as the control unit. Reagent grade lime was used to make sludge for digester 3.

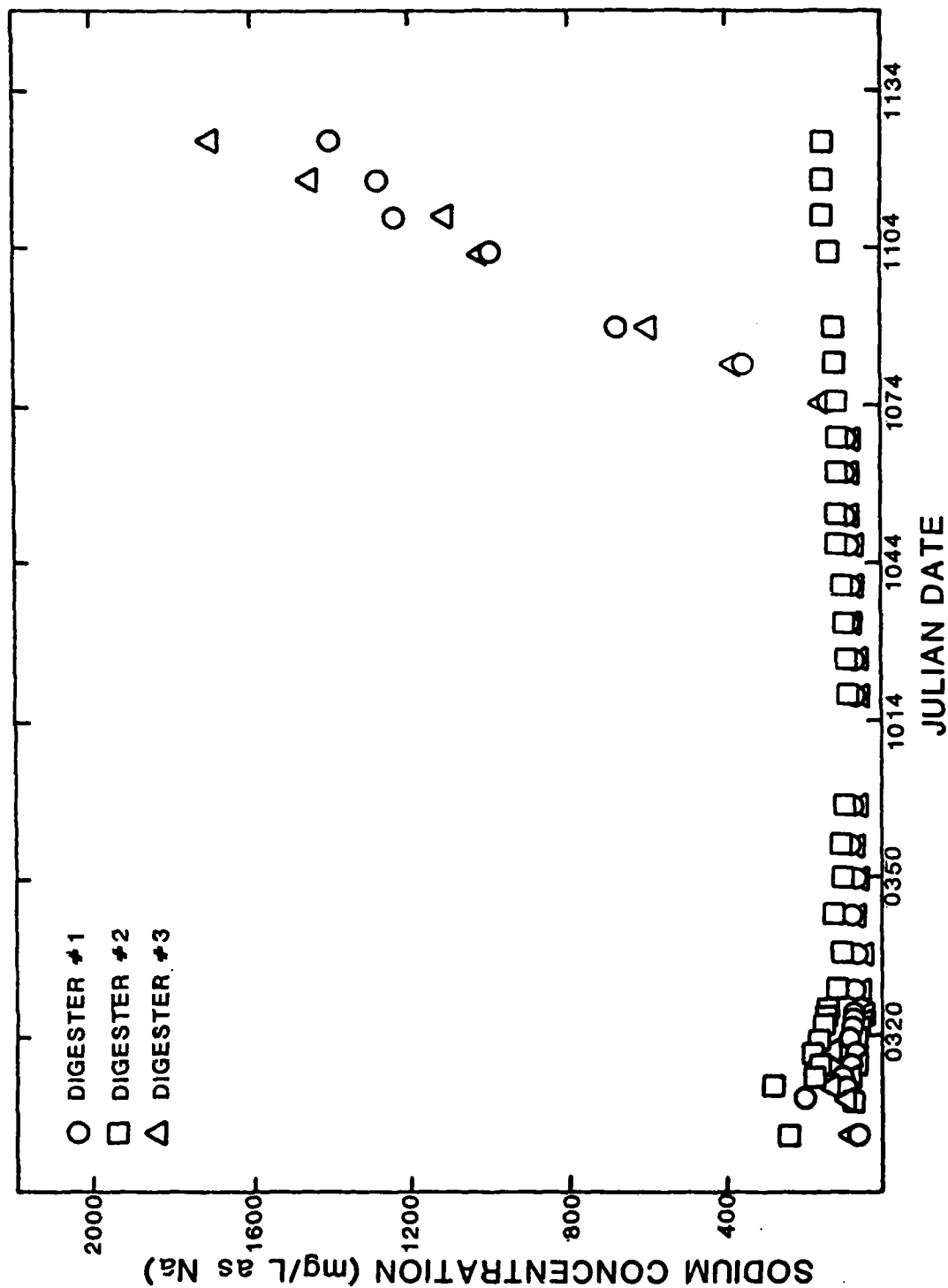


Figure 26. Sodium profiles during run 4. Commercial grade lime was used to make sludge for digester 1. Digester 2 served as the control. Reagent grade lime was used to make sludge for digester 3.

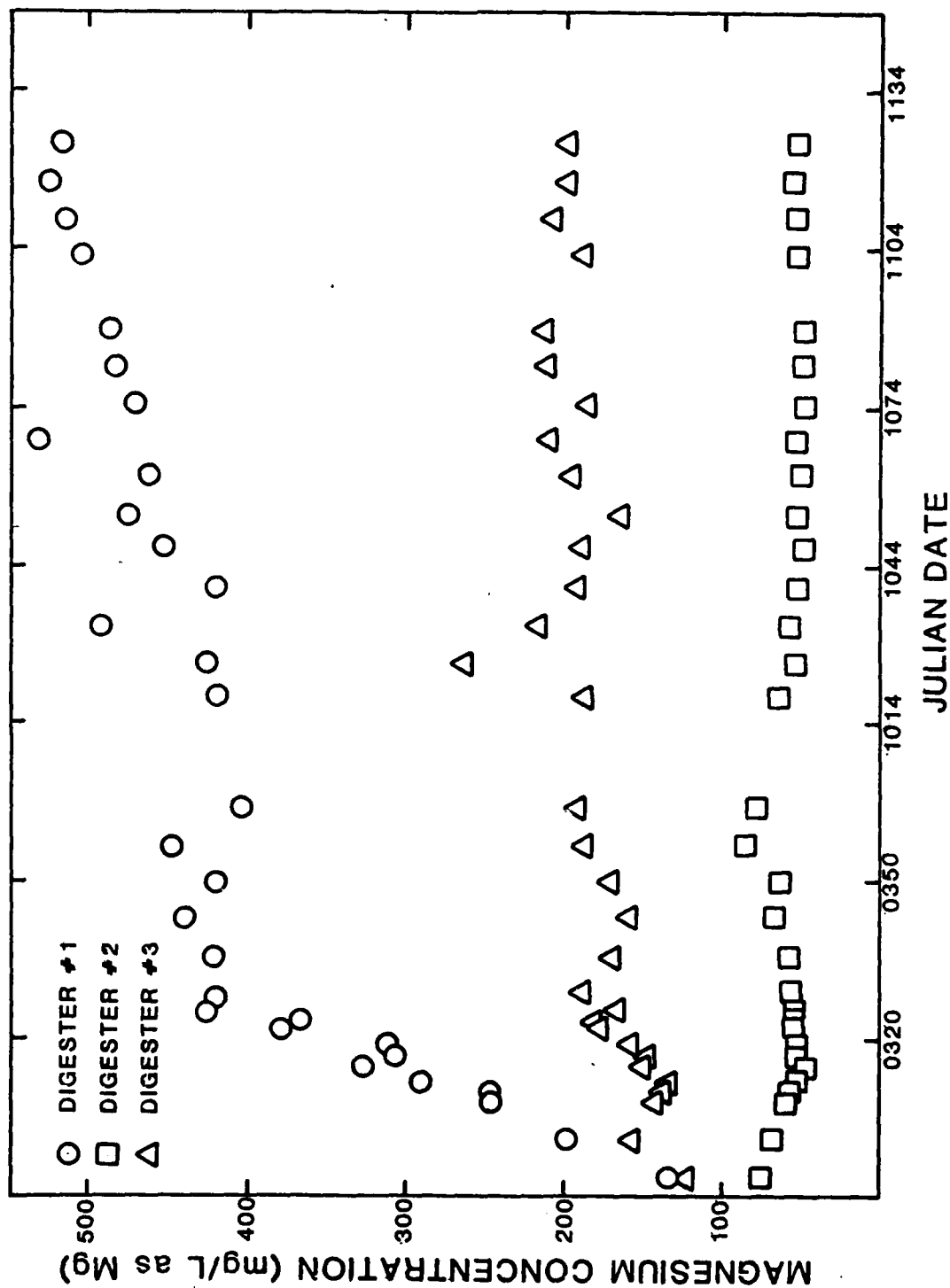


Figure 27. Magnesium profiles during run 4. Commercial grade lime was used to make sludge for digester 1. Digerster 2 served as the control unit. Reagent grade lime was used to make sludge for digester 3.

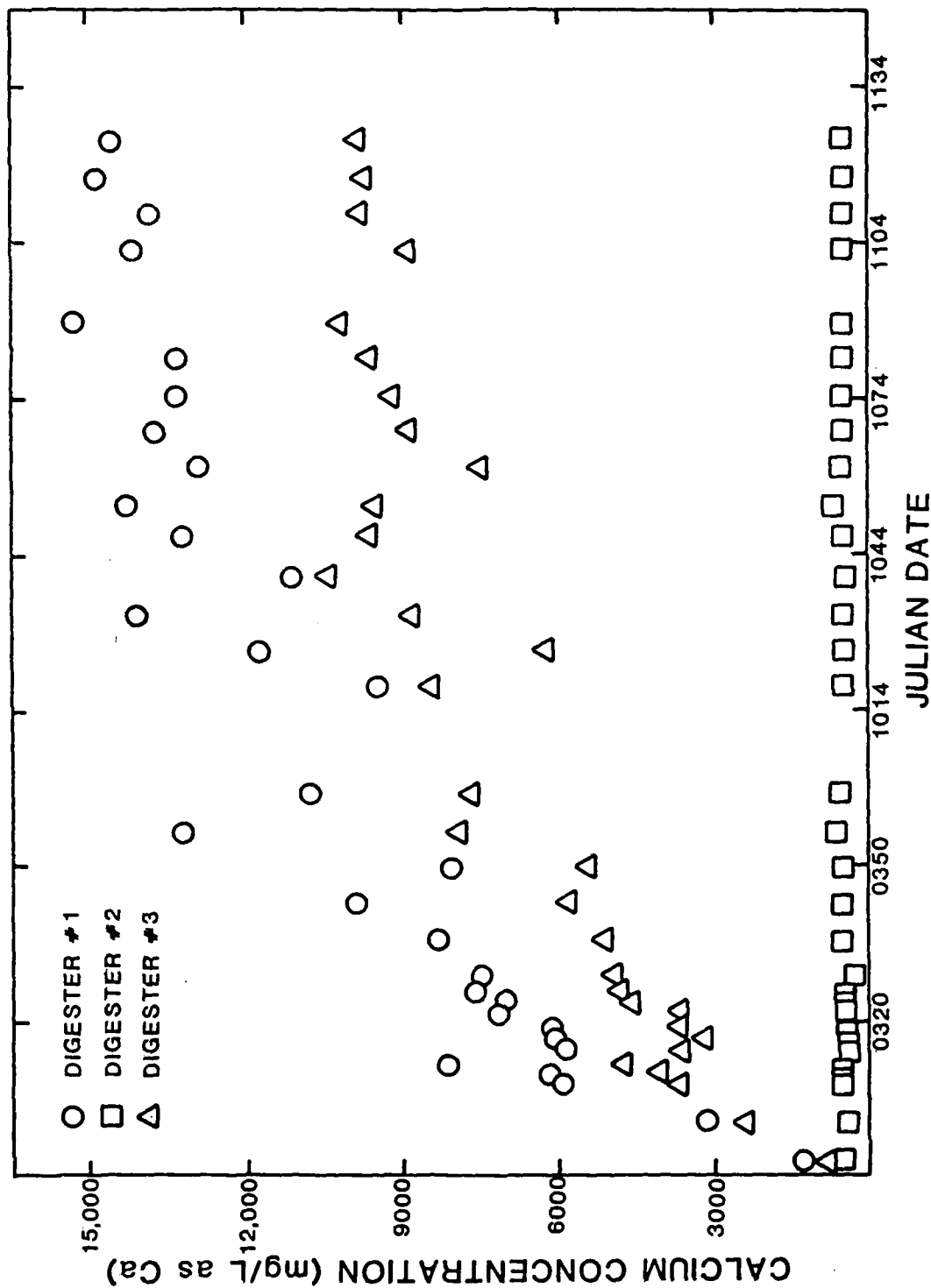


Figure 28. Calcium profiles during run 4. Commercial grade lime was used to make sludge for digester 1. Digester 2 served as the control unit. Reagent grade lime was used to make sludge for digester 3.

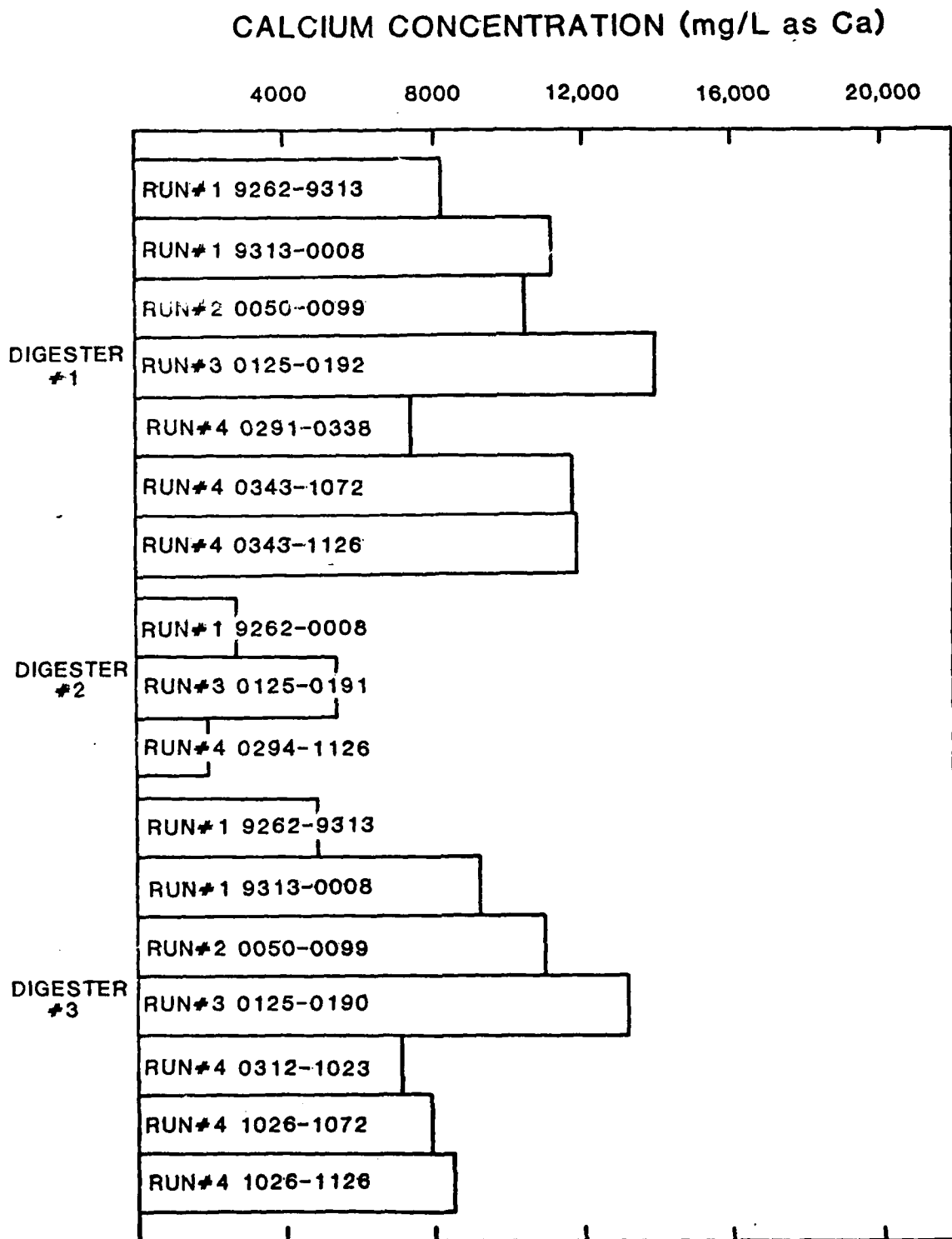


Figure 29. Average calcium concentrations for each digester. Commercial grade lime was used to make sludge for digester 1, all runs, and for digester 3, runs 1 through 3. Digester 2 served as the control unit. Reagent grade lime was used to make sludge for digester 3, run 4.



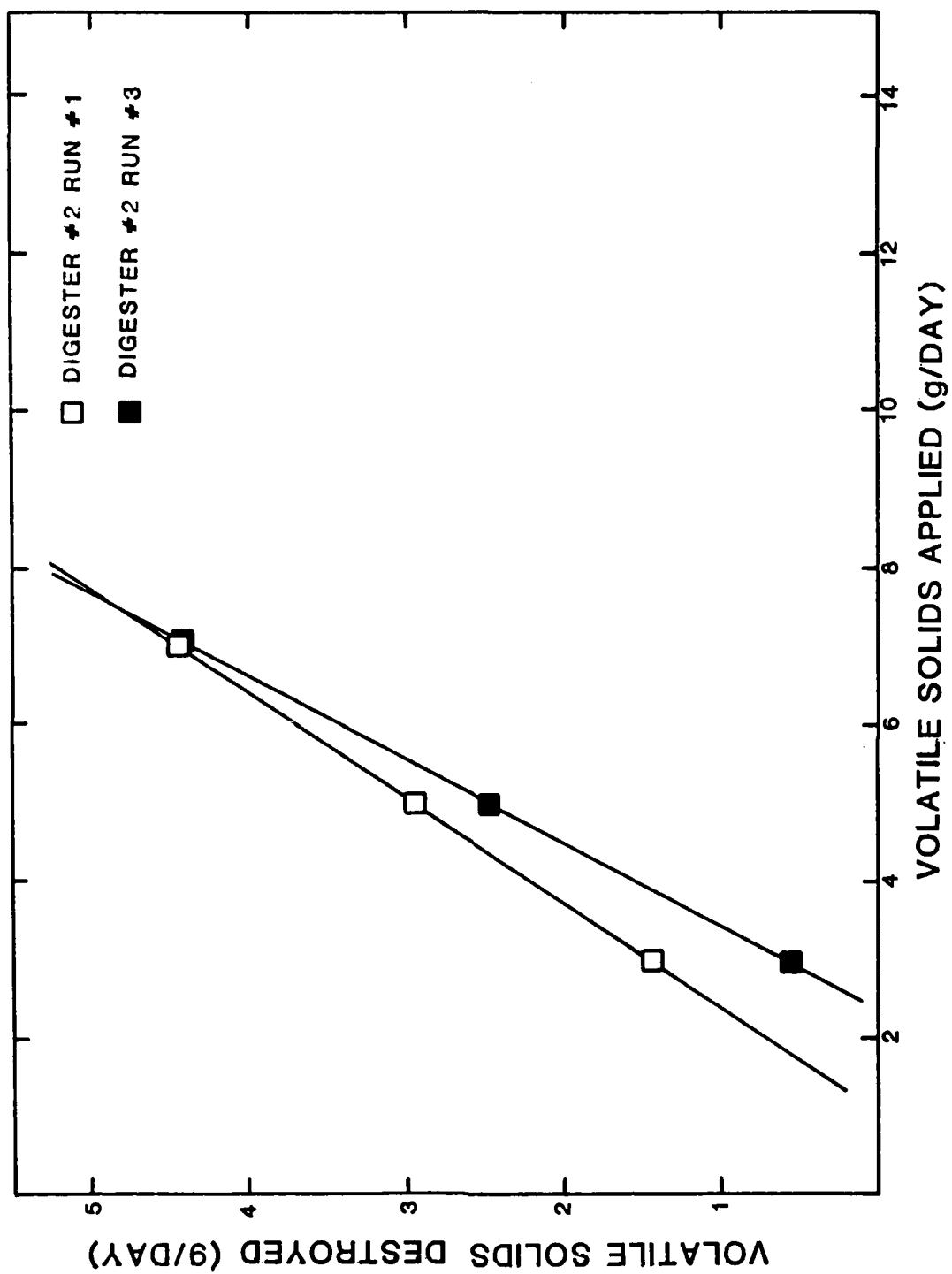


Figure 30. Volatile solids destroyed vs. volatile solids applied for digester 2, runs 2 and 3 (control units).

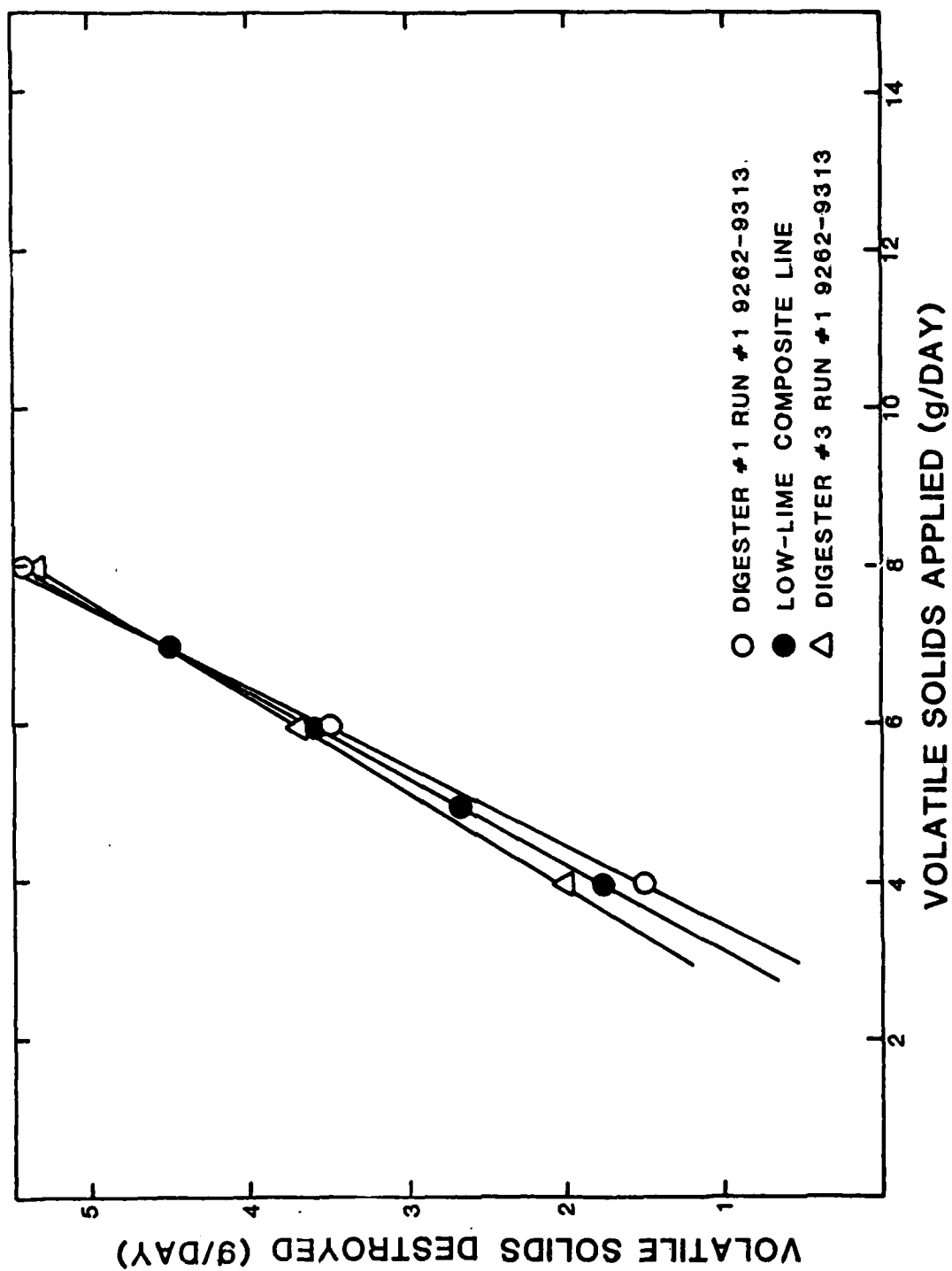


Figure 31. Volatile solids destroyed vs. volatile solids applied for low-lime concentrations (less than 8,000 mg/L as Ca), digesters 1 and 3, run 1 (9262-9313). Commercial grade lime was used to make sludge for digesters 1 and 3.

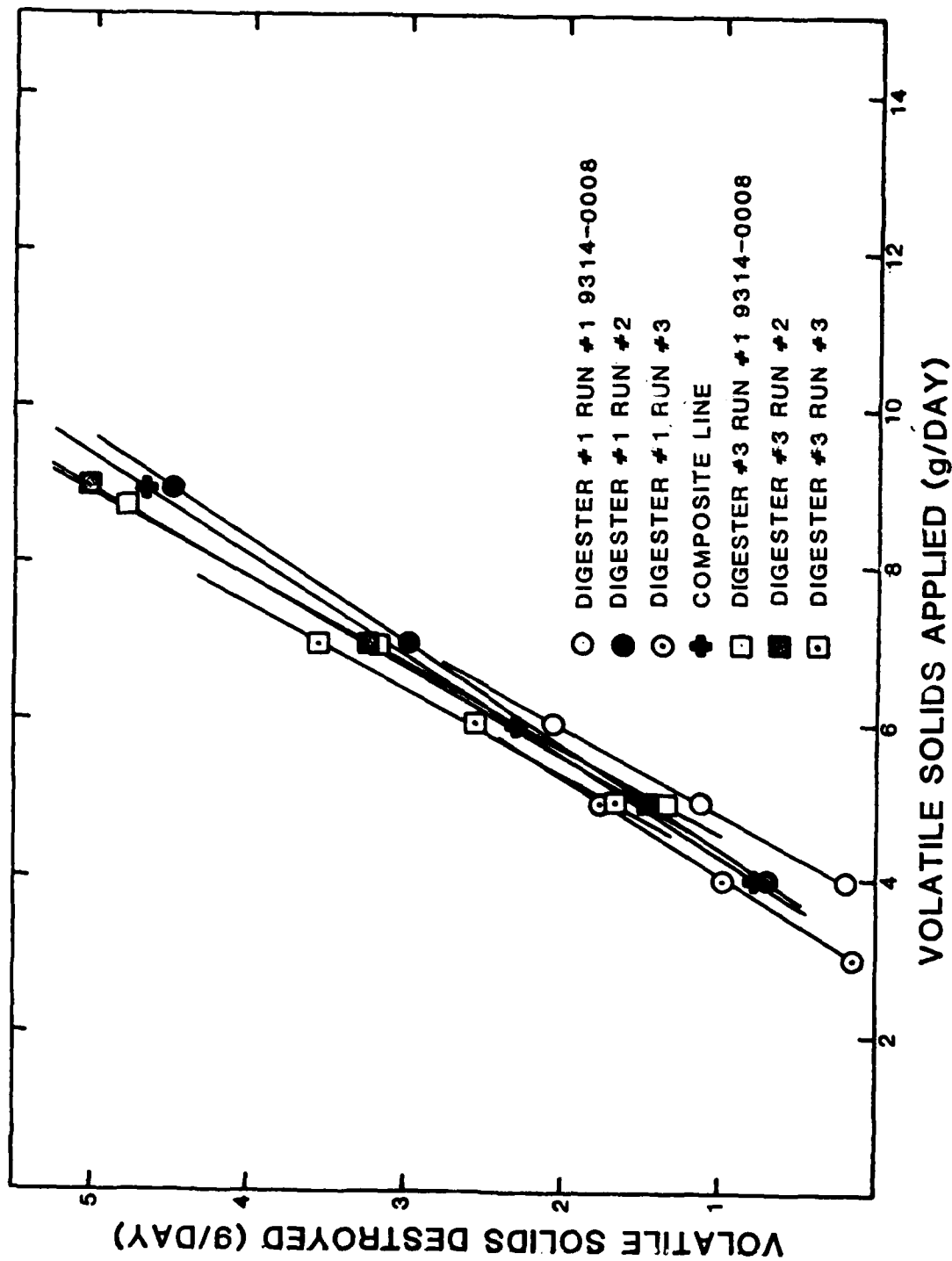


Figure 32. Volatile solids destroyed vs. volatile solids applied for high-lime concentrations (greater than 8,000 mg/L as Ca), digesters 1 and 3, runs 1 through 3. Commercial grade lime was used to make sludge for digesters 1 and 3, runs 1 through 3.

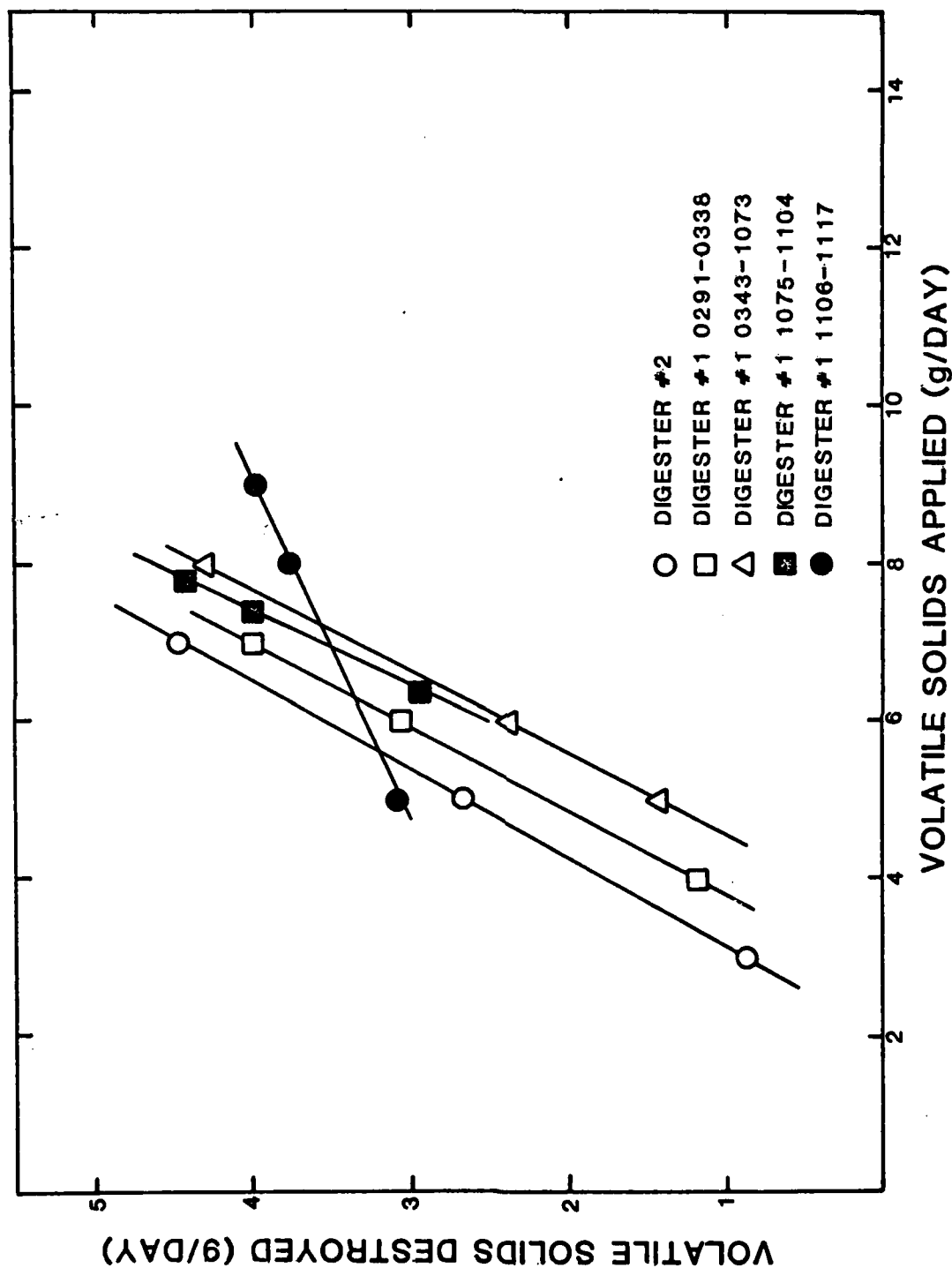


Figure 33. Volatile solids destroyed vs. volatile solids applied for digesters 1 and 2, run 4. Digester 2 served as the control. Commercial grade lime was used to make sludge for digester 1. Run 4 was broken into four segments; 1) □ Ca concentrations below 8,000 mg/L, 2) △ Ca concentrations above 8,000 mg/L, 3) ■ Ca concentrations above 8,000 mg/L and Na concentrations up to 1,000 mg/L, and 4) ● Ca concentrations above 8,000 mg/L and Na concentrations above 1,000 mg/L.

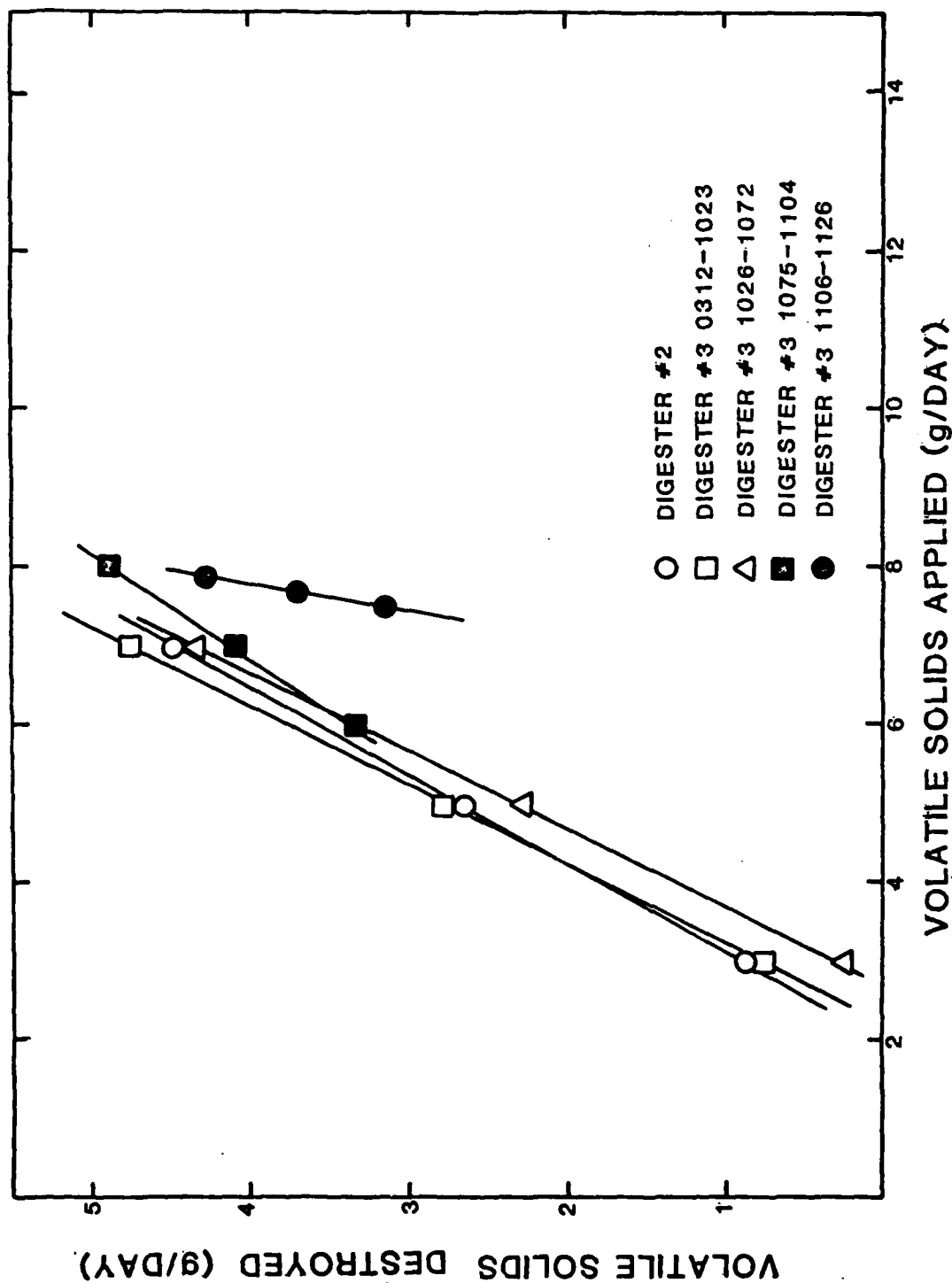


Figure 34. Volatile solids destroyed vs. volatile solids applied for digesters 2 and 3, run 4. Run 4 was broken into four segments; 1)  $\square$  Ca concentrations below 8,000 mg/L, 2)  $\Delta$  Ca concentrations above 8,000 mg/L, 3)  $\blacksquare$  Ca concentrations above 8,000 mg/L and Na concentrations up to 1,000 mg/L, and 4)  $\bullet$  Ca concentrations above 8,000 mg/L and Na concentrations above 1,000 mg/L.

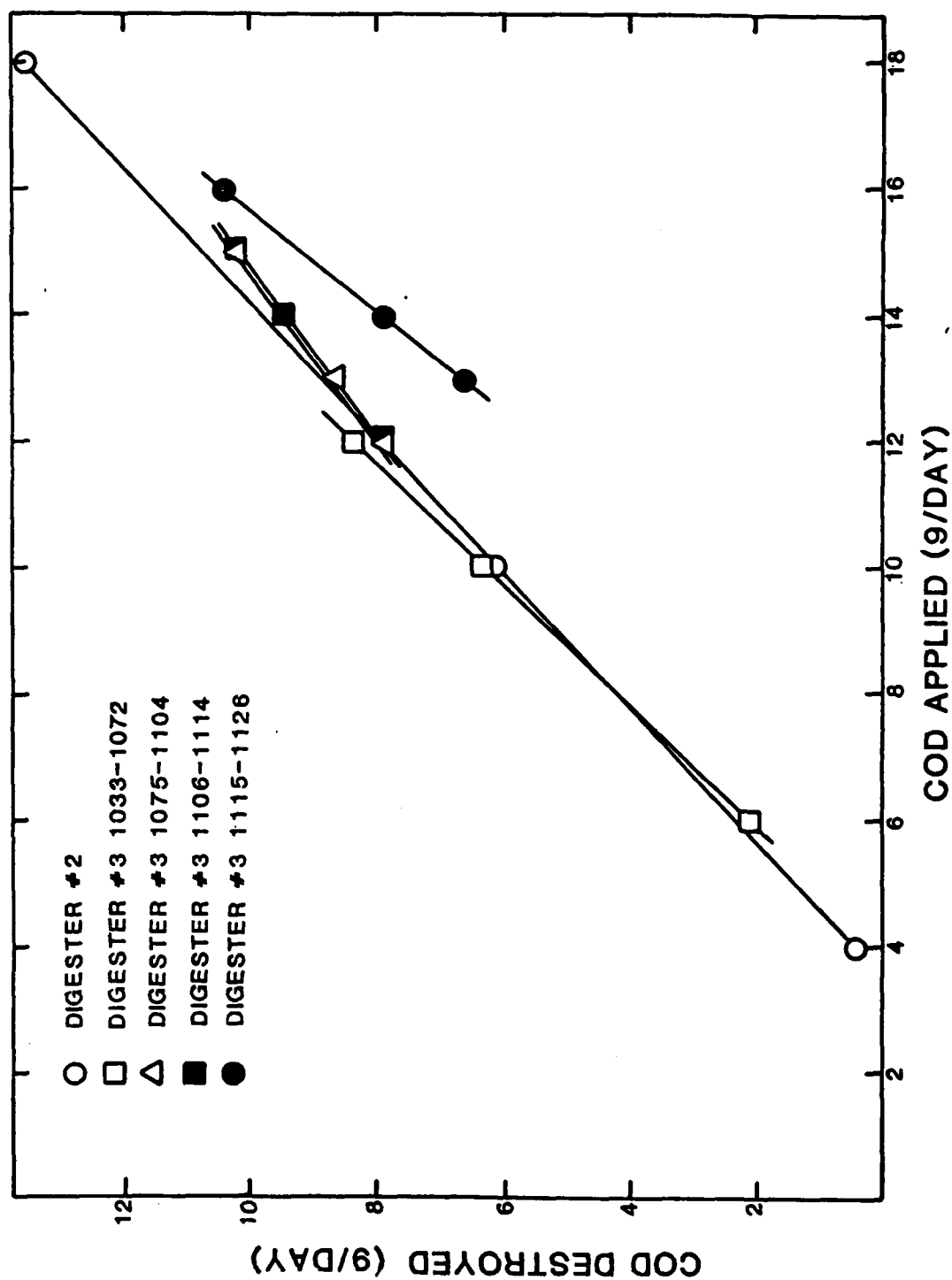


Figure 35. COD destroyed vs. COD applied for digesters 2 and 3, run 4. Digester 2 served as the control. Reagent grade lime was used to make sludge for digester 3. Run 4 was broken into four segments; 1) □ Ca concentrations below 8,000 mg/L, 2) △ Ca concentration above 8,000 mg/L, 3) ■ Ca concentrations above 8,000 mg/L and Na concentrations up to 1,000 mg/L, and 4) ● Ca concentrations above 8,000 mg/L and Na concentrations above 1,000 mg/L.

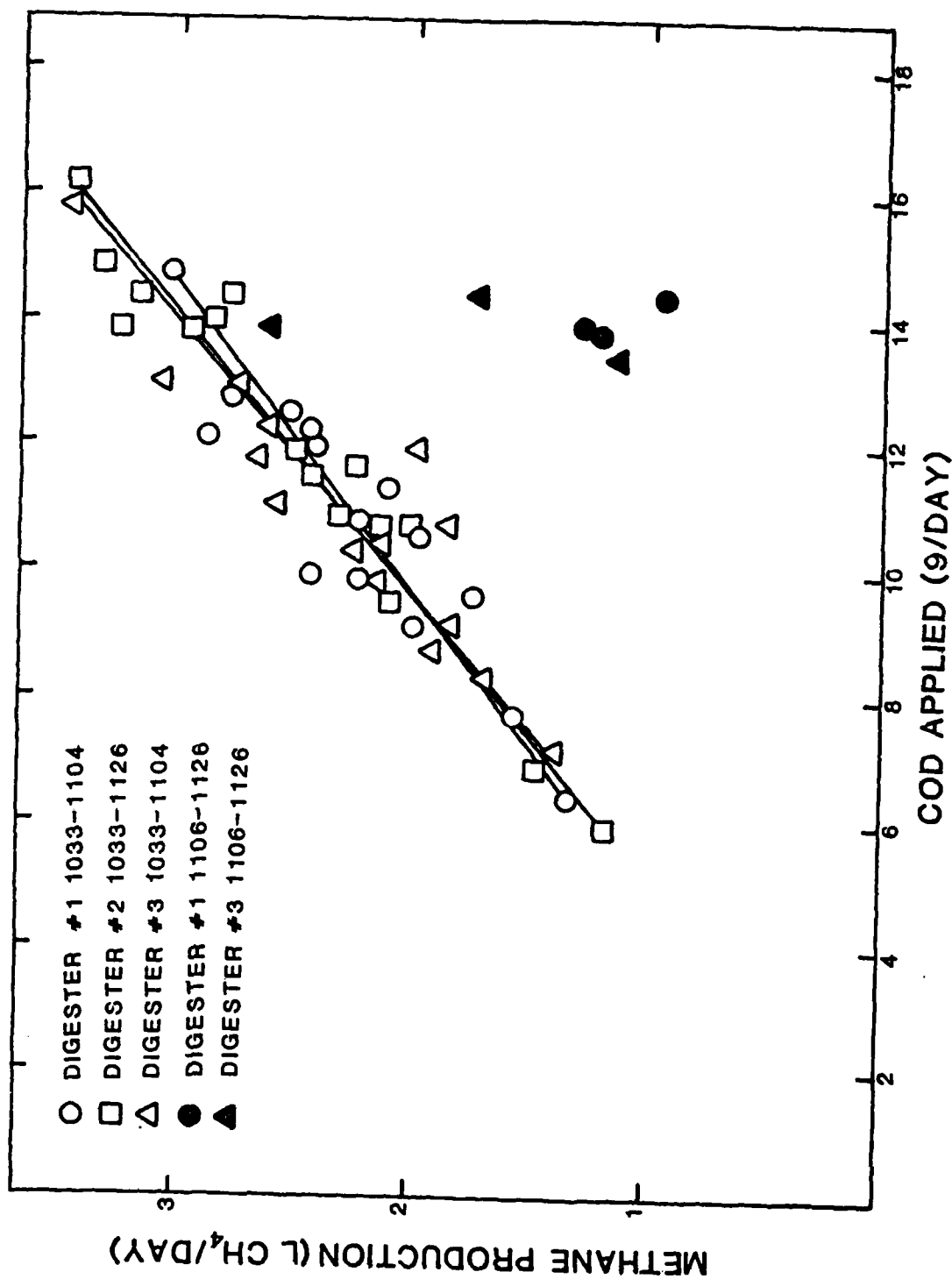


Figure 36. Methane produced vs. COD applied for digesters 1 through 3, run 4. Commercial grade lime was used to make sludge for digester 1. Digester 2 served as the control. Reagent grade lime was used to make sludge for digester 3. The ● and ▲ represent Na levels above 1,000 mg/L for digesters 1 and 3.

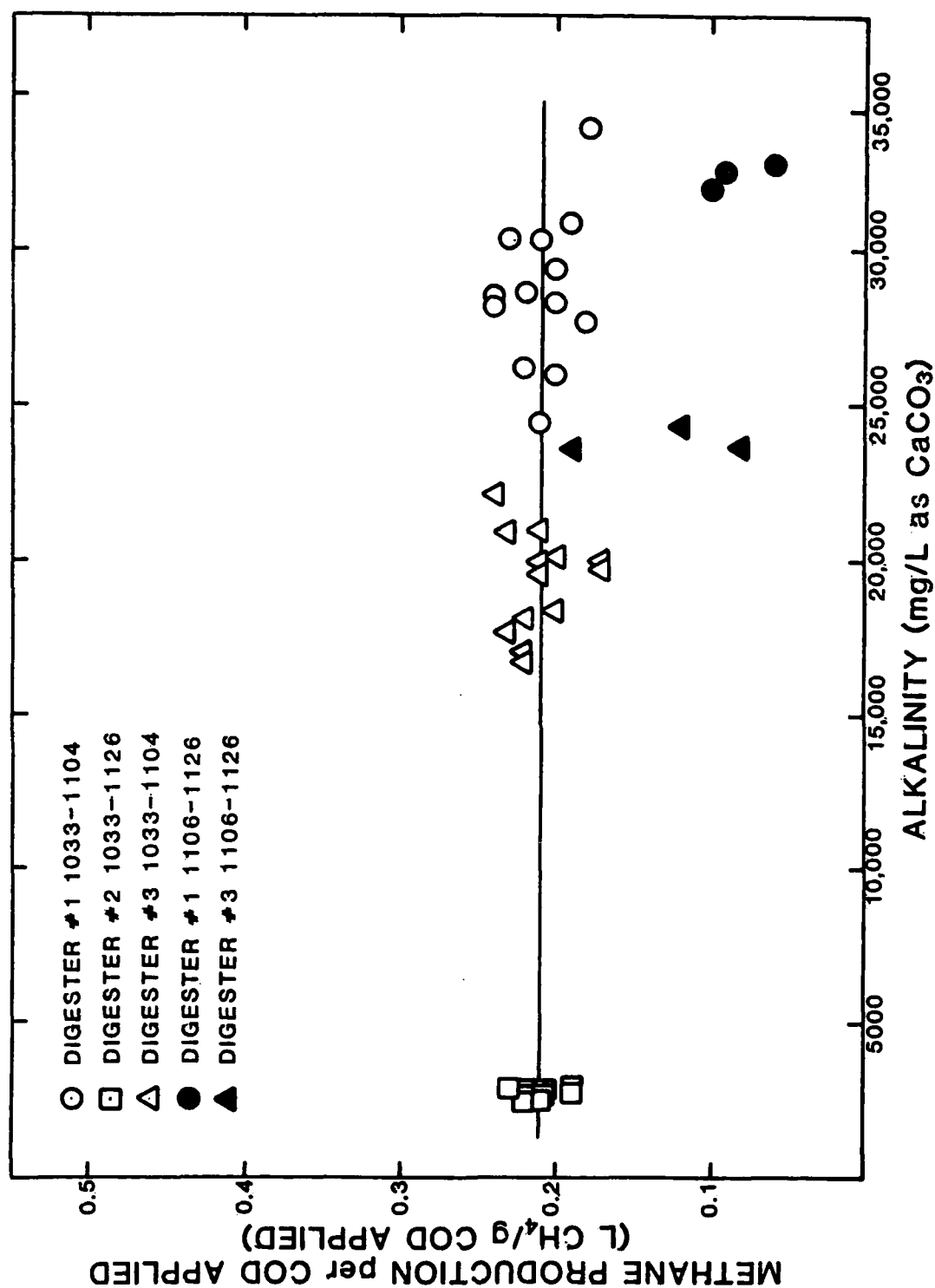


Figure 37. Methane produced per COD applied vs. alkalinity for run 4. Commercial grade lime was used to make sludge for digester 1. Digester 2 served as the control. Reagent grade lime was used to make sludge for digester 3. The ● and ▲ represent Na levels above 1,000 mg/L for digesters 1 and 3.



TABLE 14. SUMMARY OF LEAST SQUARES ANALYSIS OF GRAMS  
VOLATILE SOLIDS DESTROYED VS. GRAMS VOLATILE SOLIDS APPLIED  
DURING RUNS 1 THROUGH 4

Reactor	Run	Julian Date	Slope	Y-Intercept	R <sup>2</sup>
1	1	9261-9313	1.000	-2.509	0.828
1	1	9314-0008	0.928	-3.509	0.882
2	1	9261-0008	0.753	-0.828	0.814
3	1	9261-9313	0.832	-1.298	0.784
3	1	9314-0008	0.916	-3.223	0.805
1	2	0050-0099	0.771	-2.398	0.758
3	2	0050-0099	0.887	-2.962	0.826
1	3	0125-0199	0.801	-2.225	0.602
2	3	0125-0191	0.952	-2.274	0.702
3	3	0125-0190	0.960	-3.129	0.880
1	4	0291-0338	0.960	-2.698	0.923
1	4	0343-1073	0.961	-3.389	0.876
1	4	1075-1104	1.040	-3.704	0.779
1	4	1106-1126	0.229	+1.937	0.555
2	4	0294-1126	0.904	-1.857	--
3	4	0312-1023	0.992	-2.197	0.990
3	4	1023-1072	1.024	-2.822	0.971
3	4	1075-1104	0.758	-1.225	0.872
3	4	1106-1126	2.783	-17.724	0.490

TABLE 15. STATISTICAL COMPARISON OF SLOPES AND INTERCEPTS USING THE ANALYSIS OF VARIANCE TECHNIQUE FOR VOLATILE SOLIDS DESTRUCTION DURING RUNS 1 THROUGH 3

Comparison	Date	Slope			Intercept			Overall Comparison
		Average Difference	95% Confidence Limit		Average Difference	95% Confidence Limit		
			Lower	Upper		Lower	Upper	
Digester 1 Run 1	9262-9313							
Digester 3 Run 1	9262-9313	0.16797	-0.05046	0.38640	NSD <sup>a</sup>	-0.20762	0.07238	NSD
Digester 2 Run 1	9261-0008	-0.19842	-0.39316	-0.00367	NSD	0.58660	0.83592	D <sup>c</sup>
Digester 2 Run 3	0125-0191							D
Digester 1 Run 1	9314-0008 <sup>d</sup>	0.15762	-0.04080	0.35604	NSD	-0.23506	-0.00083	NSD
Digester 1 Run 2	0050-0099							S
Digester 2 Run 1	9261-0008							
Composite Line from 3		-0.03132	-0.12649	0.06385	NSD	1.42608	1.57849	D
Digester 2 Run 1	9261-0008							
Composite Line from 1		-0.17128	-0.31362	-0.02894	D	N/A <sup>e</sup>		D
Digester 2 Run 3	0125-0191							
Composite Line from 3		0.16710	0.01613	0.31807	D	N/A		D
Digester 2 Run 3	0125-0191							
Composite Line from 1		0.02714	-0.18587	0.24015	NSD	-0.18961	0.06917	NSD
Digester 2 Run 3	0125-0191							
Composite Line from 1								S

a. NSD = no significant difference.

b. Same.

c. D = different.

d. Comparison of highest and lowest slopes of a group of six lines representing the high levels of calcium.

e. N/A = the test is not applicable if the slope is different.

TABLE 16. STATISTICAL COMPARISON OF SLOPES AND INTERCEPTS USING THE ANALYSIS OF VARIANCE TECHNIQUE FOR VOLATILE SOLIDS DESTRUCTION DURING RUN 4

Comparison	Date	Slope			Average Difference	Result	Intercept			Overall Comparison
		95% Confidence Limit		Average Difference			95% Confidence Limit			
		Lower	Upper				Lower	Upper		
Digester 1	0343-1072									
Digester 1	1075-1104	-0.07784	-0.44567	0.28999	NS <sup>a</sup>	-0.24975	-0.43546	-0.06405	D <sup>b</sup>	D
Digester 2	0294-1126	0.64883	0.48208	0.81558	D	N/A <sup>c</sup>				D
Digester 1	0291-0338									
Digester 1	0343-1073	-0.00115	-0.21579	0.21349	NSD	0.68518	0.50653	0.86382	D	D
Digester 1	0291-0338									
Digester 1	1075-1104	-0.06773	-0.27563	0.14017	NSD	0.72904	0.55500	0.90308	D	D
Digester 1	1106-1117									
Digester 1	0343-1104	-1.35972	02.4176	-0.30186	D	N/A				D
Digester 2	0294-1126									
Digester 3	0312-1023	0.61702	0.54570	0.68840	D	N/A				D
Digester 3	1026-1072									
Digester 3	1075-1104	0.26624	0.12240	0.40960	D	N/A				D
Digester 3	0312-1023									
Digester 3	1026-1072	-0.03195	-0.09900	0.03499	NSD	0.18456	0.11858	0.25055	D	D
Digester 3	0312-1023									
Digester 3	1026-1104	0.08005	0.1694	0.14316	D	N/A				D
Digester 3	1026-1072									
Digester 3	1106-1126	-1.75885	-2.7939	00.72381	D	N/S				D

a. NSD = no significant difference.

b. D = different.

c. N/A = not applicable once slope is different.

TABLE 17. SUMMARY OF COMPOSITE LINES FROM THE  
STATISTICAL COMPARISON OF SLOPES AND INTERCEPTS  
OF VOLATILE SOLIDS DESTRUCTION  
DURING RUNS 1 THROUGH 3

Reactor	Run	Julian Date	Slope	Intercept
1	1	9314-0008		
3	1	9314-0008		
1	2	0050-0099		
3	2	0050-0099	0.785	-2.377
1	3	0125-0199		
3	3	0125-0191		
1	1	9261-9313	0.924	-1.948
3	1	9261-9313		

TABLE 18. SUMMARY OF LEAST SQUARES ANALYSIS OF GRAMS COD DESTROYED  
VS. COD APPLIED DURING RUN 4

Reactor	Run	Julian Date	Slope	Intercept	R <sup>2</sup>
2	4	0294-1126	0.939	-3.362	0.931
3	4	1033-1072	1.036	-4.167	0.685
3	4	1075-1104	0.763	-1.289	0.840
3	4	1033-1104	0.910	-2.992	0.839
3	4	1106-1114	0.746	-1.041	0.458
3	4	1115-1126	0.958	-9.985	0.886

TABLE 19. STATISTICAL COMPARISON OF SLOPES AND INTERCEPTS USING THE ANALYSIS OF VARIANCE TECHNIQUE  
FOR COD DESTRUCTION DURING RUN 4

Comparison	Date	Slope			Result	Intercept			Overall Result
		Average Difference	95% Confidence Limit			Average Difference	95% Confidence Limit		
			Lower	Upper			Lower	Upper	
Digester 3 Run 4 1033-1072									
Digester 3 Run 4 1075-1104		0.27331	-0.09874	0.64529	NSD <sup>a</sup>	0.32719	-0.29037	0.94475	NSD
Digester 2 Run 4 0294-1126									
Digester 3 Run 4 1033-1104		0.02890	-0.09888	0.15668	NSD	0.35960	0.09900	0.62017	D <sup>c</sup>
Digester 2 Run 4 0294-1126									
Digester 3 Run 4 1106-1114		0.19261	-0.67683	1.06205	NSD	0.00051	-0.58060	0.57963	NSD
Digester 3 Run 4 1033-1104									
Digester 3 Run 4 1106-1114		-0.16371	-1.04211	0.71469	NSD	0.00023	-0.67270	0.67270	NSD
Digester 2 Run 4 0294-1126									
Digester 3 Run 4 1115-1126		-0.33704	-1.05271	0.37863	NSD	1.89321	1.38850	2.39797	D

a. NSD = not significantly different.

b. S = same.

c. D = different.

TABLE 20. SUMMARY OF LEAST SQUARES ANALYSIS OF METHANE  
PRODUCED VS. COD APPLIED DURING RUN 4

Reactor	Run	Slope	Intercept
1	4	0.207	0.002
2	4	0.225	-0.168
3	4	0.231	-0.237

TABLE 21. SUMMARY OF LEAST SQUARES ANALYSIS OF METHANE  
PRODUCED PER COD APPLIED VS. TOTAL ALKALINITY  
DURING RUN 4

Reactor	Run	Slope	Intercept	R <sup>2</sup>
1	4	-0.0000022	0.27	-0.26405
2	4	-0.0000143	0.25	-0.20220
3	4	-0.0000004	0.22	-0.02994
Composite		-0.0000003	0.21	-0.02133

## DISCUSSION

During this work numerous causes of digester failure were investigated to determine the cause of apparent poor digester performance when digesting lime sludges. One common cause of digester failure is a result of unstable feed and operating conditions. During this work minor upsets did occur as a result of required equipment maintenance procedures. During replacement of internal bearings, oxygen was unavoidably introduced into the reactors. Gas production dropped immediately, due to oxygen toxicity. Data obtained during these periods were discarded until gas production levels returned to normal, indicating full recovery of the digesters.

Preliminary work performed before run 1 indicated that the lime digesters were unstable at a retention time less than 15 days. To ensure digester stability, a longer retention time (27.5 days) was chosen.

The volatile solids reduction observed for the major portion of the study, approximately 30 percent, is low when compared to an average volatile solids destruction of from 40 percent to 50 percent found for lime sludges by others<sup>17,18</sup> at comparable solids retention times and temperatures. The 30 percent volatile solids destruction found for the lime sludge digesters 1 and 3 (Fig. 38) represents less than 60 percent of the volatile solids destruction found in the control digester, digester 2. This reduction in digester efficiency, combined with the observation that the sludge was not being completely stabilized in the lime sludge digesters, leads to the conclusion that some toxicity or inhibition was experienced in the lime sludge digesters. The fact that reduction in lime digester efficiency occurred only after approximately 60 days of stabilized operation (approximately 90 days including startup) makes it appear likely that the inhibition resulted from the accumulation of a compound or compounds in the lime digesters. Since a similar reduction in efficiency was not found in the control digester, it appears likely that the inhibitory substance was either in the lime, or was more effectively concentrated in the lime sludge.<sup>12</sup>

Organic overloading was discussed earlier and may be rejected as a possible cause of the inhibition. Both heavy metal toxicity and ammonia toxicity can also be ruled out as discussed previously.

It has been suggested by at least one author<sup>31</sup> that chemically coagulated sludges may be less biodegradable than raw primary sludge. It is clear that in this study no such effect was found. Figure 38 clearly shows that during the early portion of the study (the first 60 to 90 days) the volatile solids reduction in the lime sludge digesters was superior to that found in the control digester.

Digesters 1 and 3 of run 1 maintained volatile solids destruction at approximately 60 percent over the first 60 days, Julian Dates 9362-9313, while the control digester maintained volatile solids reduction at a constant 49 percent. During start up, digesters 1 and 3 were fed raw primary sludge, until the feed rate gave a 27.5 day retention time and digester operation stabilized. After digester operation was stabilized, lime sludge was gradually substituted for the raw primary sludge over a 3-week changeover period. Run 1 officially started once the lime sludge was being used as the sole feed

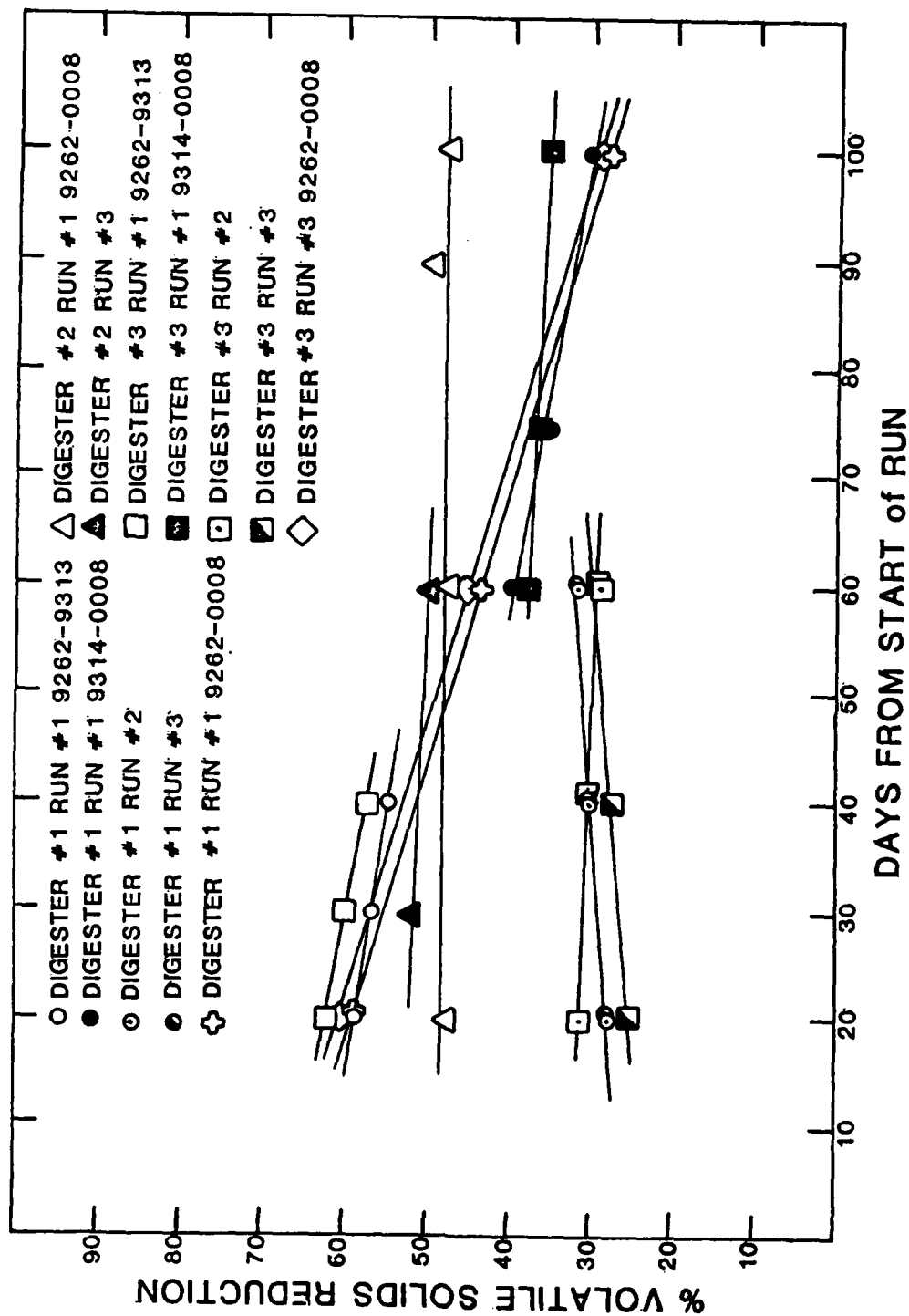


Figure 38. Percent volatile solids reduction vs. time from start of the run for runs 1 through 3. Commercial grade lime was used to make sludge for digesters 1 and 3, runs 1 through 3. Digester 2 served as the control.



source. Runs 2 and 3 did not have the long acclimation period; therefore the initial high volatile solids reduction period was not evident. Run 4 is not shown in Figure 38 because it too did not have a long acclimation period and does not demonstrate the initial high volatile solids destruction percentage.

The initial 60 days of run 1, theoretically two complete turnovers of digester contents, maintained a higher volatile solids destruction percentage (Fig. 38) than the control unit, digester 2. Thus it is apparent that the lime sludge is no less biodegradable, under favorable digester operating conditions, than the raw primary sludge.

The most likely source of the inhibition observed in the lime sludge digesters after the first 60 to 90 days operation is cation toxicity due to calcium, magnesium, or a synergism between them. As previously stated, work performed in the early 1960's has shown that light metal cations are capable of causing stimulatory, inhibitory, or toxic effects in anaerobic digesters.

In order to be certain that cation toxicity is the cause of the digester inhibition, certain other forms of inhibition and/or toxicity must be ruled out.

#### pH

The pH of an anaerobic digester is critical to proper operation. As may be seen from Figures 4 through 7, the pH of the digesters remained at all times within normal operating pH ranges. While there was some variation in digester pH during the study, it may be seen from Figures 4 through 7 that these changes were gradual and would not be expected to cause operational difficulties.

#### PHOSPHORUS

The soluble phosphate in the digesters expressed as  $\text{PO}_4\text{-P}$  was low throughout the study (Table 9). A small increase in the soluble phosphorus concentration across the digester was noted in the lime-fed digesters during all four runs. The increase in soluble phosphorus is not significant when compared to the total phosphorus load in the sludge.

Assume 1 L of sewage containing 10 mg/L of  $\text{PO}_4\text{-P}$  is treated with lime to pH 9.5. Also, assume the resulting sludge is 5 percent of the original volume and that 90 percent of the phosphorus is removed. The resultant soluble phosphorus concentration will be 1 mg/L as  $\text{PO}_4\text{-P}$ , and 9 mg of phosphorus as  $\text{PO}_4\text{-P}$  will be concentrated in the sludge. The total phosphorus concentration then becomes 180 mg/L insoluble  $\text{PO}_4\text{-P}$  plus 1 mg/L soluble  $\text{PO}_4\text{-P}$  (a total of 181 mg/L  $\text{PO}_4\text{-P}$ ). The possible re-release of a few mg/L  $\text{PO}_4\text{-P}$  is not significant.

In all cases the effluent phosphorus concentration from digesters 1 and 3 was lower than the effluent concentration from digester 2 (control digester). Recirculation of the digester supernatant from lime sludge digesters to the head of the plant, therefore, results in a lower recycle phosphorus load than from recycle of supernatant from anaerobic digestion of sludges from conventional treatment processes.

## AMMONIA

Ammonia may result in beneficial, adverse, or no effect on anaerobic digestion. The ammonia concentrations in all digesters were in the range yielding beneficial or no adverse effects (Table 10). The analytical methods used did not involve digestion or distillation of the sample to ensure complete ammonia recoveries in runs 1, 2, and 3; however, the samples were distilled prior to analysis during run 4. It is apparent that the ammonia concentration in runs 1 through 3 is sufficiently low so that the revision in analytical technique will not raise the measured concentrations of ammonia to values within the inhibitory or toxic range.<sup>9</sup> Therefore, it is clear that ammonia toxicity is not responsible for the decrease in digester efficiency.

## VOLATILE ACIDS

The normal operating range for volatile acids in anaerobic digesters is 200 to 800 mg/L as acetic acid.<sup>32</sup> As may be seen in Figures 8 through 11, the volatile acid concentration remained at or below the normal operating range except just prior to total digester failure as a result of excessive sodium addition. Because of oxygen exposures during maintenance, the volatile acids did rise at certain times above 800 mg/L. Therefore, volatile acid toxicity is not the cause of the inhibition.

## GAS PRODUCTION

The gas production was highly variable as a result of large variations in digester loading. Drops in gas production, such as in reactor 2 during run 4 (Fig. 21) may be explained due to required maintenance on the internal mixing mechanism. During this maintenance, air was introduced into the digester.

In the latter part of run 3 and all of run 4 the average gas composition corresponded to values expected from the literature.<sup>9,18</sup> Some variation was seen in the gas quality, but this is a normal occurrence. Exposure to oxygen and organic loading changes induce a gas quality change. After maintenance was completed and the organic load variations ended, the gas quality returned to normal values.

## LOADING

Digester upsets and failures have been noted as a result of organic overloads.<sup>9,11-13</sup> Typical design volatile solids loadings for mesophilic, high-rate anaerobic digesters are from 1,600 to 6,400 grams volatile solids per day per cubic meter of digester capacity. The lime sludge digesters (digesters 1 and 3) were loaded in the range of 170 to 976 grams volatile solids per day per cubic meter of digester capacity. The average loadings were from 407 to 558 grams volatile solids per day per cubic meter of digester capacity for digesters 1 and 3. The control digesters had an average loading from 286 to 623 grams volatile solids per day per cubic meter of digester capacity.

Inspection of Figures 30 through 34 indicates that volatile solids destruction vs. volatile solids applied follows a linear relationship. This indicates that the systems are not overloaded. If the systems were overloaded, the lines would reach a maximum and volatile solids destruction would begin to level off.

From the above it is clear that organic (volatile solids) overloading may be eliminated as the cause of reduced lime sludge digester efficiency.

#### HEAVY METALS

The heavy metals scan at the end of run 3 (Table 12) indicates that heavy metal toxicity was not the cause of digester inhibition. At no time during run 4 did the heavy metals concentration approach the severely inhibitory range; therefore, heavy metals poisoning may be ruled out as a cause of the inhibition shown in Figures 30 through 34.

#### VOLATILE SOLIDS DESTRUCTION

The method of operation utilized during runs 1 through 3 resulted in the data representing one long run for each digester, rather than three independent runs. The digester effluent removed daily that was not required for analysis was mixed and stored. At the end of the first run, the sludge from all three digesters was mixed with the sludge stored during the run and used as a seed to start the digesters for run 2. This practice was repeated for the subsequent start-up of run 3. Run 4 was started with fresh sludge from the Hagerstown sewage treatment plant.

The practice of mixing and reusing the sludges resulted in one long run with different steady-state plateaus, as may be confirmed by inspection of Figures 32 and 38 and Tables 15 and 17. In Figures 32 and 38 it may be observed that volatile solids reduction as a function of applied load is statistically identical for the lime digesters from Julian dates 9314 to 0199. The buildup of alkalinity in all three digesters as the study proceeded is shown in Figure 23. The increase in alkalinity observed in each succeeding run would not be expected had new sludge been used to initiate each run. This is apparent from data obtained from the control unit, digester 2. No increase in alkalinity with each run would be expected. The increase observed may be attributed to the alkalinity contained in the lime digester effluents which were mixed with control digester effluent and used as a seed to start runs 2 and 3. For these reasons, the data from all three runs will be treated as a single run for purposes of discussion and interpretation.

It is apparent from inspection of Figures 30 through 34, Figure 38, and Table 17 that the rate of volatile solids destruction initially decreases as the duration of the run lengthens. Digesters 1 and 3 of run 1 show a marked decrease in volatile solids destruction after approximately 60 days into the run (90 days including startup). The volatile solids destruction rate then remains constant at a much lower value as indicated by the shift to the right of the operations line in Figures 30 through 34 and as indicated by the downward shift of the operations lines in Figure 38.

A preliminary cation scan performed at the end of run 3 shows elevated calcium and magnesium levels (Table 22). During run 4 the light metal cations, Na, Mg, K, and Ca, were monitored. The potassium levels were well below the inhibitory levels presented in Table 3. Magnesium concentrations of up to 500 mg/L (0.02 M) were observed in reactor 1 (commercial lime). Reactor 3 had magnesium concentrations of 200 mg/L (0.008 M), while the control unit consistently ran at 50 mg/L (0.002 M) magnesium. Sodium levels remained constant at approximately 100 mg/L until Julian date 1075, when

NaHCO<sub>3</sub> additions were begun to raise the sodium level. Calcium levels in reactor 1 approached 15,000 mg/L (0.37 M) and 10,000 mg/L (0.15 M) in reactor 3 by the end of run 4.

TABLE 22. PRELIMINARY CATION SCAN  
AT THE END OF RUN 3

Cation	Concentration (mg/L)			
	Lime Sludge Digester #1		Control Digester #2	
	Soluble	Total	Soluble	Total
Calcium	233	19,500	153	7,490
Magnesium	229	529	62	218

Kugelman and McCarty<sup>15</sup> defined many antagonistic and synergistic cation combinations as well as single cation 50 percent inhibition levels. Calcium exhibits a 50 percent inhibition at 0.11 M (4,400 mg/L as Ca), while magnesium exhibits a 50 percent inhibition at 0.08 M (1,900 mg/L as Mg). Magnesium levels in digesters 1 and 3 never reached the 50 percent inhibition level, whereas the calcium levels exceeded the 50 percent inhibition level. The calcium/magnesium pair both in digesters 1 and 3 fall within the synergistic system range. The synergistic and toxic cation levels taken from the Kugelman and McCarty paper were derived for enrichment cultures of acetate utilizing methanogenic bacteria only.<sup>15</sup>

Volatile solids destruction for the four runs may be broken into three operating regimes: 1) control (no lime addition), 2) low calcium concentrations, and 3) high calcium concentrations. A definite shift in the volatile solids destroyed vs. volatile solids applied line occurred at a calcium concentration of approximately 8,000 mg/L. A comparison of the control units of runs 1 and 3 reveals that only run 1 was a true control. Digester 2 run 3 has a considerable amount of calcium (Fig. 23); enough calcium to begin to cause a shift in the operating line (Fig. 30). Figure 30 shows a definite reduction in digester efficiency as measured by volatile solids reduction, which was statistically verified in Table 15. The only major difference between run 1 and run 3 on reactor 2 was the average total alkalinity and hence the calcium concentration (Figs. 23 and 29). The calcium levels of run 3 lie in the moderately inhibitory zone (Table 3). The average calcium concentrations are 2,757 mg/L for run 1 and 5,443 mg/L for run 3.

The next comparison to be made is between volatile solids destruction for digester 1 and digester 3 during the first part of run 1, Julian dates 9262 to 9313. Figure 31 shows that the two lines are nearly identical, and statistical analysis shows that the two lines can be considered the same (Table 15). Average calcium concentrations of 8,140 mg/L for reactor 1 and 4,931 mg/L for reactor 3 (Fig. 29) when compared to Table 3 show that the reactors are operating in a calcium inhibitory regime.

A comparison of volatile solids destruction for digester 1 during runs 1, 2, and 3, and digester 3 during runs 1, 2, and 3 on Figure 32 yields a statistically significant composite line. The lines with the highest and lowest slopes were compared and did not differ significantly as to slope or intercept (Table 15). When comparing the calcium levels of Figure 29 to Table 3, one sees that the six operating lines all lie in the strongly inhibitory zone. Calcium concentrations greater than 8,000 mg/L do not seem to add to the inhibition.

The reduction in volatile solids destruction efficiency increased with increasing calcium concentration up to approximately 8,000 mg/L. As may be seen in Figure 32, at calcium concentrations between 8,000 and 15,000 mg/L, the inhibition of volatile solids reduction becomes constant.

Figure 39 shows a comparison of the composite low and high calcium level operating lines with the control (digester 2, runs 1 and 3). Digester 2, run 3 and the composite line for low calcium levels are statistically identical (Table 15). In general, Figure 39 shows that as the average calcium concentration is increased, the efficiency of the digester decreases.

Figure 33 compares volatile solids destruction for digester 1, run 4, to the control digester for run 4. Digester 1 was run on sludge generated by commercial lime additions to pH 9.5. During the low-level calcium phase, Julian dates 0291-0338, an average of 7,060 mg/L as Ca was present. From Julian dates 0343-1073, calcium levels averaged 11,891 mg/L. The efficiency of volatile solids destruction was considerably decreased, as is indicated by the shift of the lines to the right. The control, low-level lime, and high-level lime lines were tested statistically and found to be different (Table 16). During the time period Julian dates 1075-1104, the sodium concentration was increased to a level of 1,000 mg/L as Na. The time period Julian dates 1106-1117 had sodium values greater than 1,000 mg/L as Na and the volatile acids were increasing.

Table 14 presents the curve fit data and statistical comparison of the slope and intercept of volatile solids destroyed versus volatile solids applied. The low-level calcium, high-level calcium, and less than 1,000 mg/L sodium lines all have statistically equal slopes according to the 95 percent confidence limits set on the test (Table 16). Only the slope for the control line is different.

Volatile solids destruction for digester 3, run 4 is compared to the run 4 control in Figure 34. Sludge for reactor 3 was produced using reagent grade lime additions to pH 9.5. During the period Julian dates 0312-1023, an average calcium level of 5,298 mg/L Ca was maintained. The low-level calcium line appears to be identical to the control line but the statistical analysis (Table 16), shows that they are indeed different lines. Julian dates 1026-1072 represent the high levels of calcium, with an average value of 8,727 mg/L as Ca. The high-level calcium line is parallel to the low-level calcium line and has a different intercept. The line representing high calcium levels and a sodium level of less than 1,000 mg/L covers Julian dates 1075-1104. This line is significantly different from the high calcium level line without sodium addition. After Julian date 1104, the sodium additions continued, and digestion performance further deteriorated, as demonstrated by the line Julian dates 1106-1126.

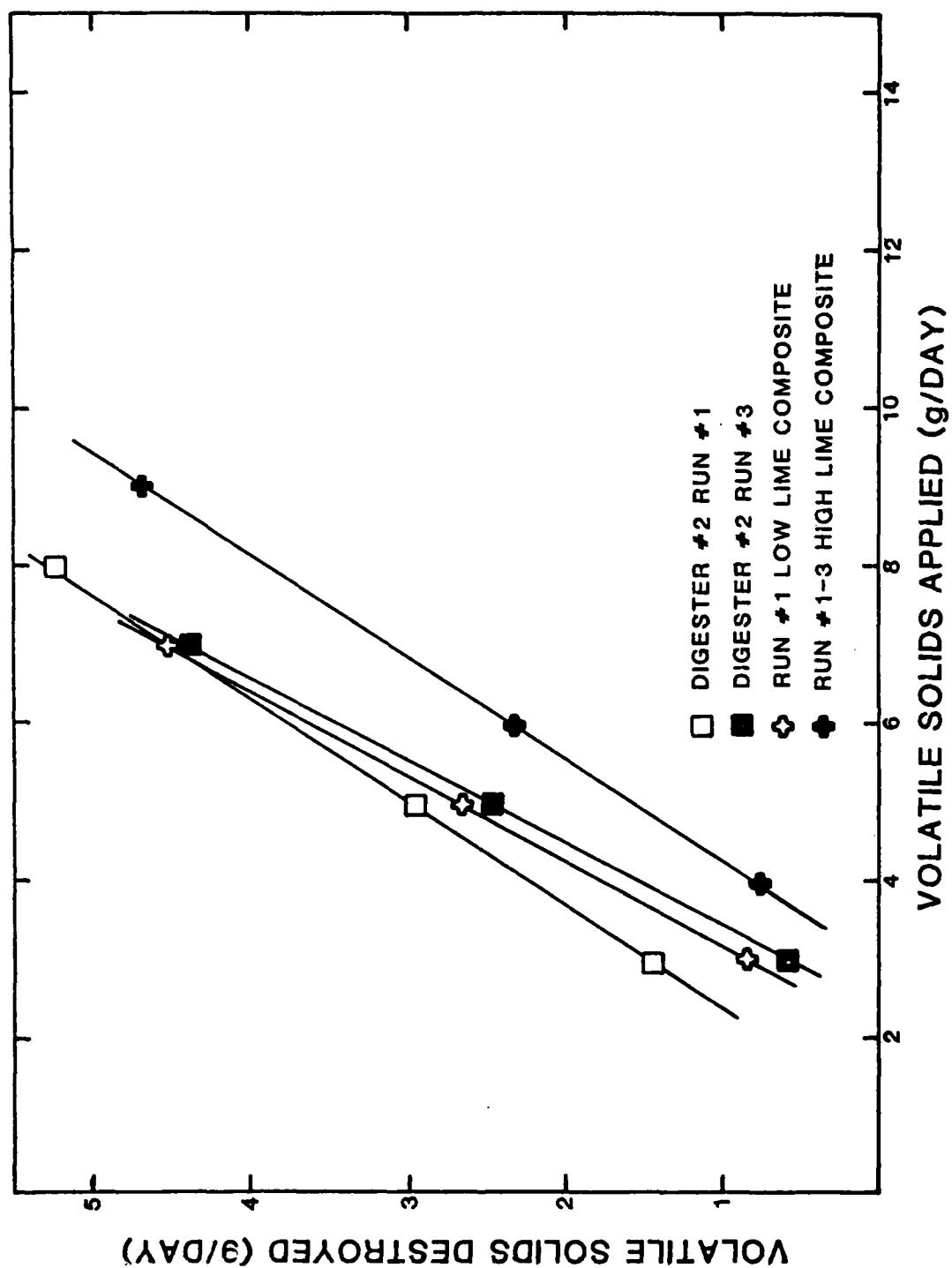


Figure 39. Summary of volatile solids destroyed vs. volatile solids applied for runs 1 through 3. Digester 2 served as the control unit. Commercial grade lime was used in the runs to generate the low and high lime composites.

In general, digesters 1 and 3 exhibited the same pattern of behavior although the high calcium levels of digester 1 were not reached in digester 3. The only difference between the two systems was the level of magnesium. Reactor 1 maintained magnesium levels between 400-500 mg/L (Fig. 27), whereas reactor 3 maintained a 200 mg/L magnesium level throughout the study. The higher magnesium levels in digester 1 could have been enough to produce a synergistic pair between calcium and magnesium.

A comparison between runs 1 through 3 and run 4 must be made to demonstrate the reproducibility of conditions within the systems. The control reactors are compared in Figure 40. Digester 2, run 1 and run 4 are identical. This suggests that the basic characteristics of the raw sludge over the 2-year time period are constant.

The next major comparison, Figure 41, is between reactors containing low levels of calcium (less than 8,000 mg/L as Ca as suggested by Table 3). The trend: the higher the calcium level the farther the line is displaced to the right, continues to hold except in the case of digester 3, run 4. Digester 3, run 4 has much lower magnesium levels, which appear to retard the inhibition. Therefore, calcium and magnesium must form a synergistic pair.

The high-level calcium lines are compared in Figure 42. The composite line from runs 1 through 3 and reactor 1, run 4 overlap. The average calcium level for reactor 1, run 4 is 11,900 mg/L as Ca, while the average calcium level computed from Figure 29 is 11,500 mg/L for the composite line from runs 1 through 3. Reactor 3, run 4 does not exhibit the same degree of inhibition. This is probably due to the lower magnesium levels; however, the calcium level, 8,700 mg/L as Ca, is considerably less than for the other two lines and may be in a transitory area.

Figure 43 is a plot of percent volatile solids destroyed vs. total alkalinity. This figure is based on an average load of 5.24 grams volatile solids/day (which is an average of the average loads for all runs). The percent volatile solids destroyed is calculated from the data in Figures 30 through 34. Figure 23 presents the average alkalinity used for each digester and run. Once again the dependence on alkalinity (calcium concentration) is evident. As the alkalinity increases, the efficiency of volatile solids destruction decreases. A significant break in the line occurs at approximately 17,000 mg/L total alkalinity, which translates to 7,500 mg/L as Ca.

The evidence thus far indicates that the acid formers are primarily affected. As calcium levels increase, volatile solids destruction decreases. Only the acid formers effect volatile solids destruction. This is further supported by the fact that during the portions of run 4 before sodium additions and runs 1 through 3, the levels of volatile acids remained in the normal operating range. Only after sodium addition did the volatile acids concentrations approach or reach toxic levels. If the methanogenic bacteria were primarily affected, the volatile acids should have rapidly increased and eventually caused digester failure before excessive concentrations of sodium were present.

Sodium was added to the reactors in an attempt to reverse or lessen the inhibition. Calcium or magnesium forms an antagonistic pair with sodium.<sup>14,15,25,26</sup> The antagonism was not evident at any sodium concentration

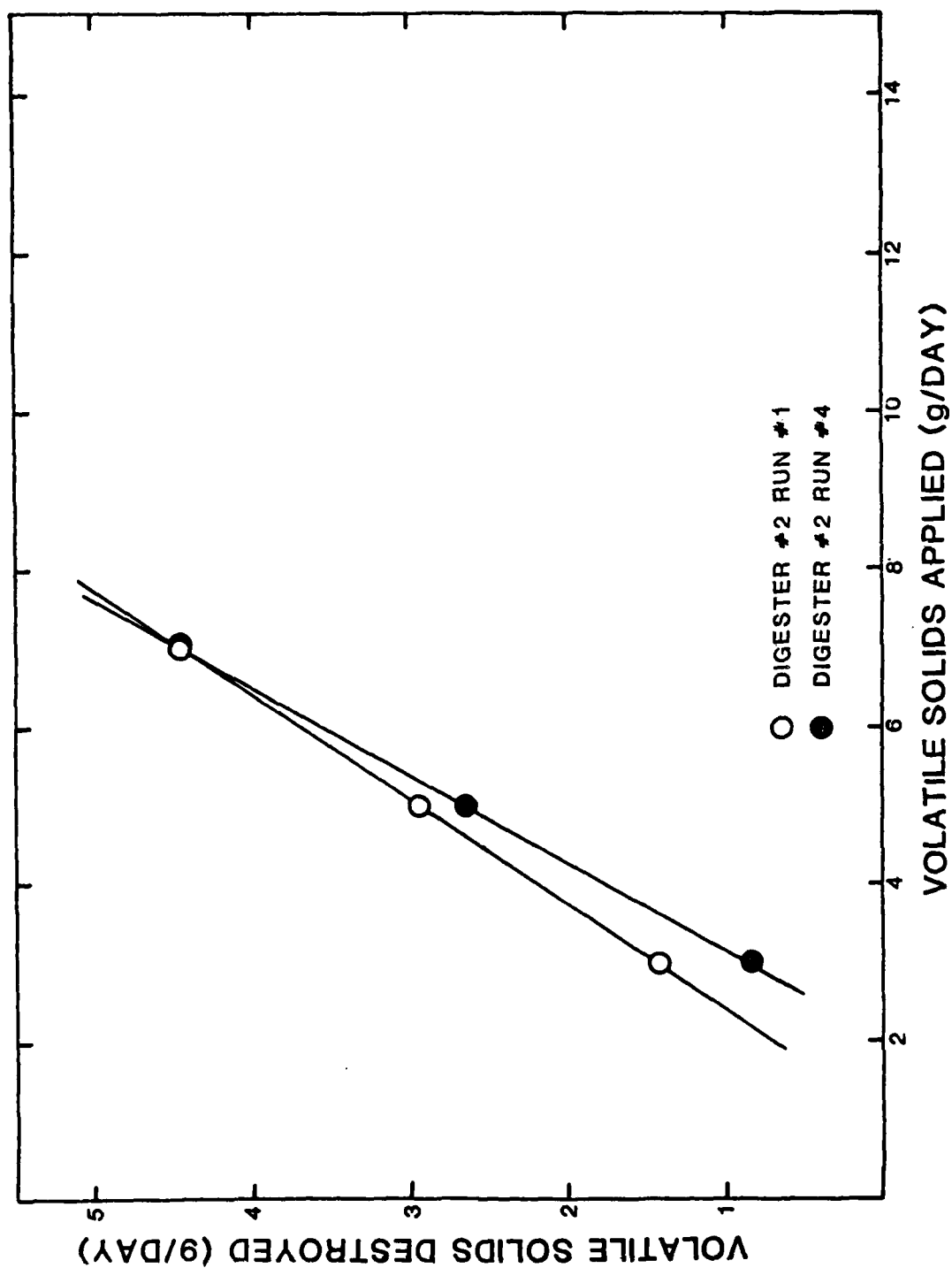


Figure 40. Comparison of volatile solids destroyed vs. volatile solids applied for the control digesters.



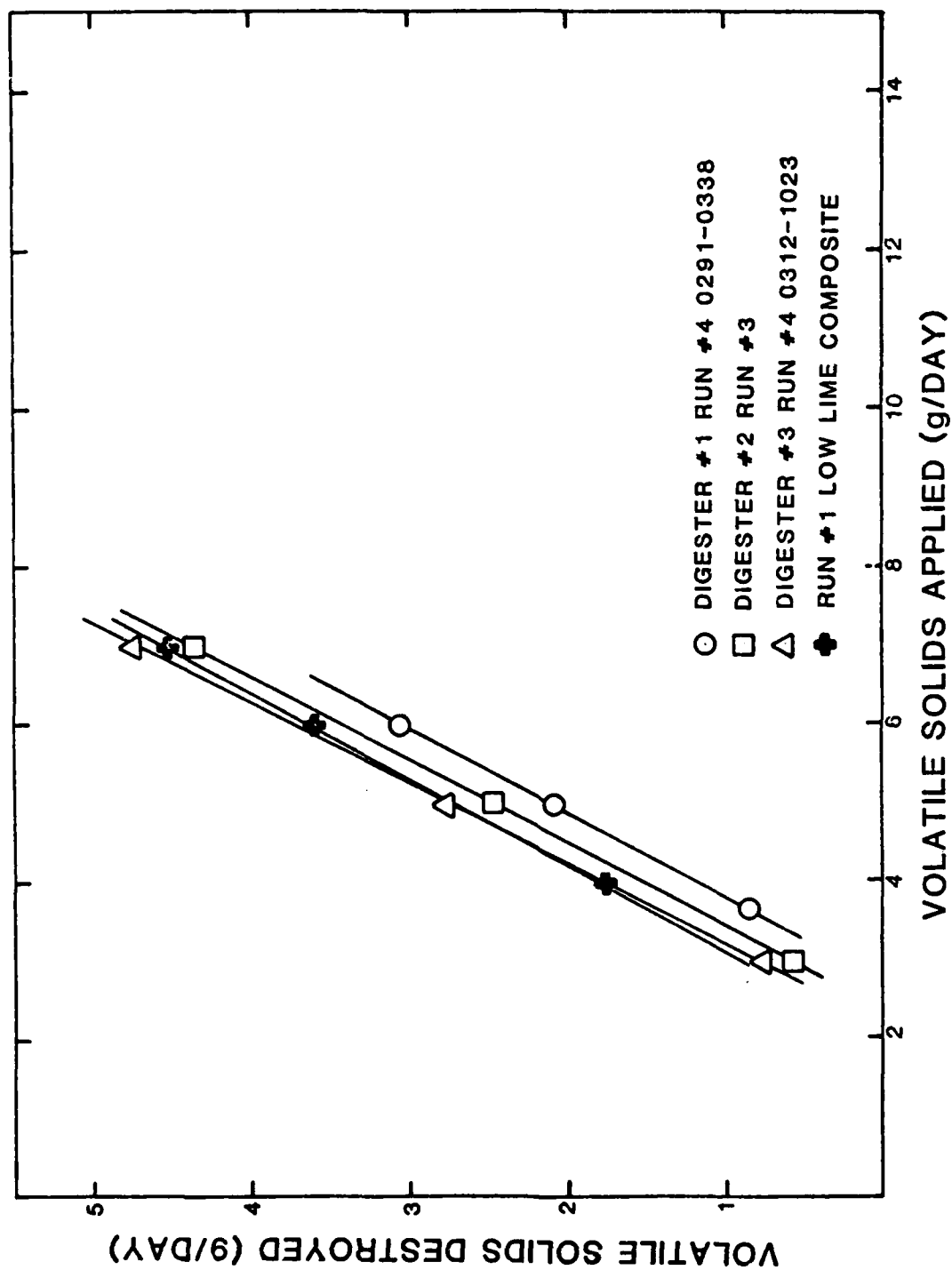


Figure 41. Comparison of volatile solids destroyed vs. volatile solids applied for low calcium concentrations. Commercial grade lime was used to make sludge for digester 1 and both digesters in the run 1 low lime composite. Digester 2 was the control for run 3. Reagent grade lime was used to make sludge for digester 3.

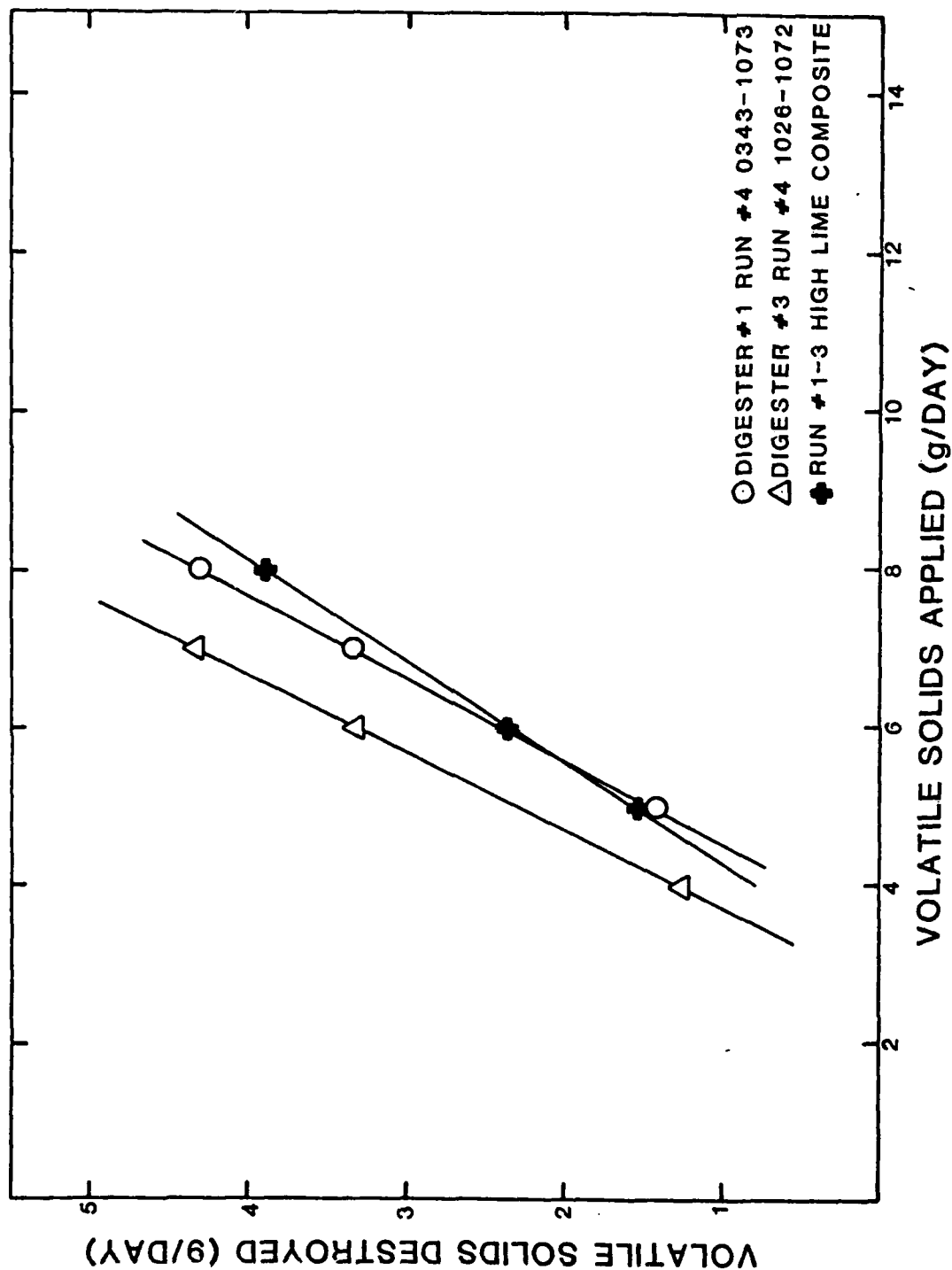


Figure 42. Comparison of volatile solids destruction vs. volatile solids applied for high calcium concentrations. Commercial grade lime was used to make sludge for digester 1 and all digesters in the high lime composite. Reagent grade lime was used to make sludge for digester 3.

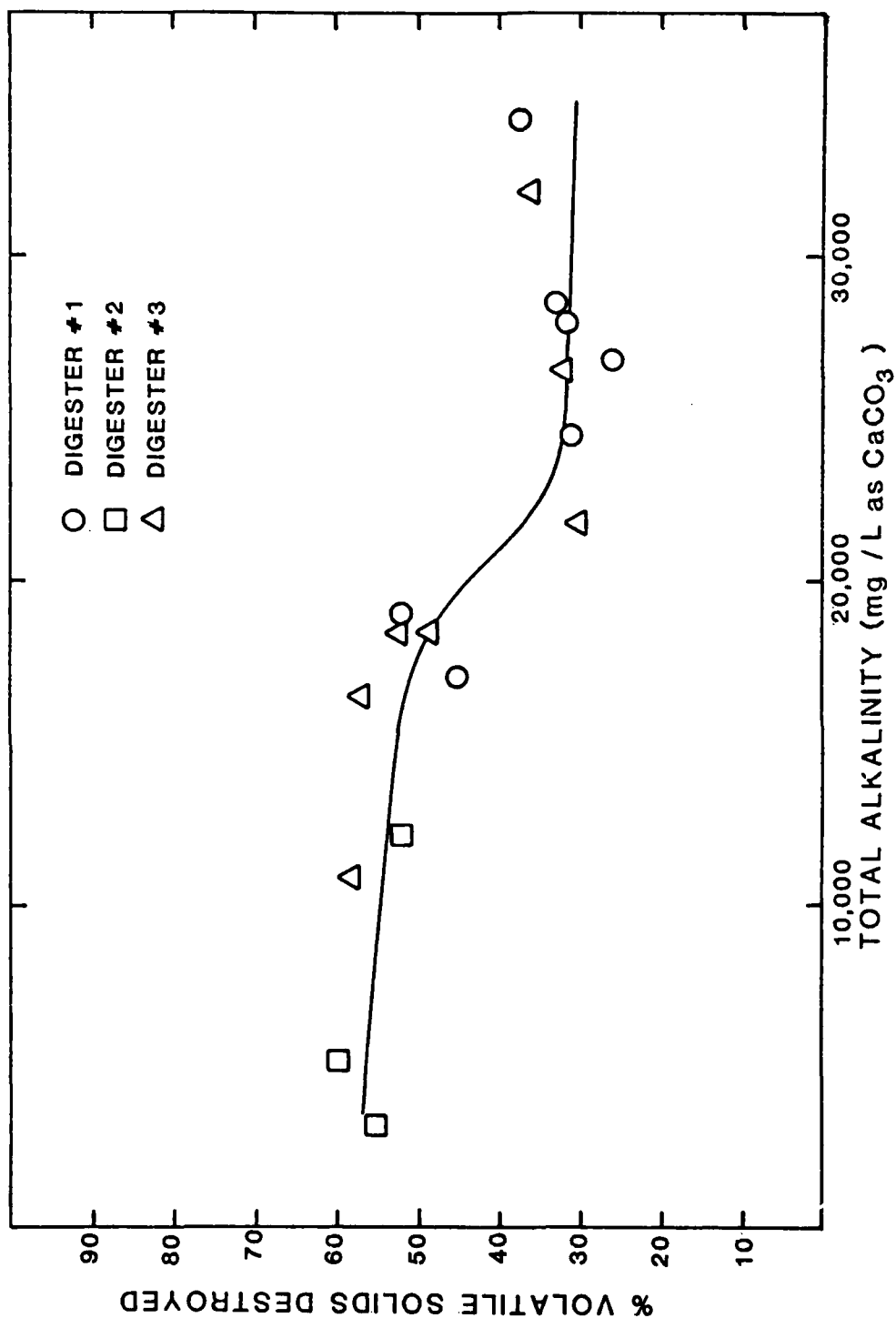


Figure 43. Percent volatile solids destroyed vs. total alkalinity based on an average loading of 5.24 grams volatile solids per day. The equations used to calculate the points were taken from Table 14.

up to 1,000 mg/L (0.04 M). Sodium levels above 1,000 mg/L began to cause an increase in volatile acids (Fig. 11) and a decrease in volatile solids destruction as shown in Figures 33 and 34. It is clear that sodium or synergistic sodium/calcium toxicity occurs at levels greater than 1,000 mg/L as sodium. At this sodium level, digester failure occurs.

#### COD

Previous investigations<sup>15,25</sup> indicate that inhibition of methane formers, and, therefore, of COD destruction may occur due to cation toxicity. This result was not found in the current study. The destruction of COD as a function of applied load (Fig. 35) remained constant at all calcium and magnesium concentrations. Statistical analysis supports this observation (Table 19).

The addition of high levels of sodium (>1,000 mg/L), however, does result in inhibition of methanogenic bacteria. This may be seen from Figure 35 and verified by the statistical analysis in Table 19.

Conversion of COD to methane also was not affected. The linear relationships between volume of methane produced per day and COD applied are identical for all three digesters (Fig. 36). Once the sodium levels exceed 1,000 mg/L, the efficiency of COD conversion drops off (Fig. 36). To further verify the lack of calcium/magnesium inhibition, a comparison of methane produced per gram COD applied versus alkalinity (calcium) was made and is shown in Figure 37. As may be seen from Figure 37 and Table 21 the methane produced per gram of COD applied is independent of alkalinity (calcium) for each individual reactor as well as the composite. Therefore, no inhibition to methanogenic bacteria was observed in this study up to alkalinities of 35,000 mg/L as  $\text{CaCO}_3$  (15,000 mg/L as Ca).

McCarty and Kugelman<sup>15,25</sup> have reported that high calcium and magnesium levels inhibit methanogenic bacteria. However, their work was done in enrichment cultures of methanogenic bacteria, not on the acid formers. The conclusions drawn from Figures 35, 36, and 37 showing COD and volatile solids destruction versus applied load as a function of cation concentration do not necessarily conflict with the previous work.

Consider the mechanism of methane formation:

Organic matter  $\xrightarrow[\text{hydrolysis}]{\text{acid formers}}$  volatile acids

Volatile acids  $\xrightarrow{\text{methane formers}}$  methane +  $\text{CO}_2$

If methane formation is upset, volatile acids build up, and the process fails. If the acid formation step is upset, a reduction in volatile solids destruction occurs, and the process does not fail. The relative importance of acid formation versus methane formation must be determined. At retention times less than 10 days, methane formation is the rate limiting step.<sup>33</sup> At retention times greater than 15 days, hydrolysis of the precursor organic material for subsequent acid formation is the limiting step. With a 27.5-day retention time, the experimental runs are all in the hydrolysis limiting regime. Since a larger-than-needed methanogenic population is present, it is

possible to inhibit both the acid formers and methane formers at unequal rates and still maintain a system in equilibrium. Calcium can be added in larger concentrations until the rate of acid formation exceeds the rate of acid destruction and the process fails. The process can then survive at a greatly reduced volatile solids destruction efficiency, until the rate of acid destruction becomes less than the rate of acid formation.

#### CONCLUSIONS

1. Inhibition of volatile solids destruction was shown to be dependent upon the calcium levels up to 8,000 mg/L of Ca.
2. Volatile solids destruction inhibition appears to become constant between 8,000 and 15,000 mg/L as Ca.
3. Some synergistic effect of magnesium was noted on the inhibition of volatile solids destruction.
4. No antagonism to the inhibition of volatile solids destruction due to sodium addition up to 1,000 mg/L as Na was noted.
5. Synergism with calcium inhibition was noted, causing digester failure at sodium levels greater than 1,000 mg/L as Na.
6. No inhibition of methane formers was noted at any calcium concentrations up to 15,000 mg/L as Ca.
7. In a system treating lime sludge, inhibition of the acid formers due to calcium and/or magnesium was sufficient to mask any inhibition of methane formers which may have been present.
8. Despite high lime additions, the pH in all lime fed digesters remained in the range normally found for anaerobic digestion.
9. No significant resolubilization of phosphorus during digestion was observed.
10. Lime sludge is as biodegradable as raw primary sludge; however, the digested lime sludge is not completely stabilized.

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